

INDUSTRIAL CHEMISTRY

BY

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TO
MY WIFE
ROXIE CLARK READ
WHO HAS
"HELD THE FORT"
UNTIL THE COMPLETION
OF THE PRESENT TASK
THIS BOOK IS
AFFECTIONATELY DEDICATED

PREFACE

The purpose of this book is to give an adequate and well-balanced picture of modern industries from the standpoint of chemical compounds and changes, chemical engineering operations, sources of raw materials, uses of products, and economic relationships.

The first section deals with topics that need to be discussed before any specific process is studied. The arrangement of subjects in the remainder of the book is based on the chemistry of processes rather than the uses of products.

Students preparing for a career in chemical industry need a broad picture of all those industries concerned with chemistry. An increasing number of students who do not expect to enter a chemical field would like to know more about the applications of chemistry to industry. Teachers of chemistry in high school and college should be sufficiently familiar with chemical industries to give accurate information about essentials, even though in their courses time permits only the briefest of references to industrial processes. Business men are often in need of condensed information about a process or a product, and many are interested in a general survey of modern chemical industries. This book is written with a view to meeting the needs of all these classes of readers. It is intended as a text book and as collateral reading for students, and as a reference book for business men.

The author has taught courses in industrial chemistry for a number of years, and regards such courses as cultural and informative and in no sense taking the place of instruction in the fundamentals of chemistry and chemical engineering. This book is the outgrowth of an accumulation of lecture notes since 1919.

Recognizing that no one man, either from personal experience or reading, can write with authority about the multitude of processes in chemical industry, the author has submitted every chapter in this book to authorities in the respective fields. Ninety different individuals have had a part in the revision of the final manuscript.

The author has no desire to publish an impressive list of reviewers, since his inquiries as to the accuracy of his statements were private and confidential. It is in no sense a lack of gratitude that causes this

omission. When an authority in a technical field makes a statement for which he is willing to stand responsible, he wishes to use his own language and to have adequate space to make his meaning clear.

Illustrations for students and other readers inexperienced in chemical technology should be simple line-drawings, preferably cross sections, and adequately provided with explanatory legends. The type of drawing used by Badger and McCabe in "Elements of Chemical Engineering" was selected as best suited for this book, and a number of firms were asked to prepare drawings of this kind with the addition of lettered explanations. The response to this request was most gratifying; the larger part of the drawings reproduced in this book were contributed.

Statistics of production have not been brought up to date because of unsettled conditions in industry. In some cases figures have been given, and in others no attempt has been made to go beyond

W. T. READ

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INDUSTRIAL CHEMISTRY

CHAPTER I

THE RELATION OF CHEMISTRY TO INDUSTRY

The term "Industrial Chemistry" generally refers to the application of the science of chemistry to industry, and thus includes the whole field of chemistry and chemical engineering. The point of view is primarily that of use and applications. The field is ordinarily limited to those industries whose plants are centrally located, to which raw materials are brought, and from which products are sent to their users.

The late Dr. John E. Teeple has defined a chemical industry as one that has these four characteristics:

1. It must produce something chemically different from the raw material which it uses.
2. The preponderance of all operations in the manufacture of its products must involve chemical changes.
3. Its processes must be in charge of chemically trained operators.
4. The business direction of the industry must be in the hands of men of chemical training and outlook.

This definition excludes a very considerable number of industries that depend on chemistry. Furthermore, there has been a very extensive penetration of chemistry and chemical engineering into industries that once were regarded as unrelated to chemistry. For this reason the field of industrial chemistry as covered in this book is broader than that of chemical industry.

The Census of Manufacturers has grouped a number of industries under the heading "process industries," which classification includes for the most part those industries with which chemistry and chemical engineering are concerned. Following are the process industries groupings from the Census of Manufacturers,

- A. Chemicals and Chemical Preparations.
- B. Ceramics, Brick and Clay Products.
- C. Coke.
- D. Drugs, Medicines, and Cosmetics.
- E. Explosives and Fireworks.
- F. Fertilizers.
- G. Glass.
- H. Gelatin, Glue, and Adhesives.
- I. Leather.
- J. Lime and Cement.
- K. Gas.
- L. Oils and Greases, Animal and Vegetable.
- M. Paints and Varnishes.
- N. Paper and Pulp.
- O. Petroleum Refining.
- P. Rayon.
- Q. Rubber Goods.
- R. Soap.
- S. Sugar.
- T. Other Process Industries.

It is well to recognize at the outset that there are these three classes of industries:

1. Chemical Industries.
2. Industries in which chemical changes take place, but in which such changes are not the preponderating characteristics of the whole process.
3. Industries in which no important chemical change takes place, but which employ chemistry in standardization and improvement of products.

Strictly chemical industries include the manufacture of what are commonly called "heavy chemicals" and "fine chemicals." "Heavy chemicals" is a term that applies to such products as the common acids, soda ash, caustic soda, and those salts that are produced in large quantities and at relatively little cost. Their production involves chemical change, separation, and purification. Some solvents and reagents are now made synthetically at low cost, but more often solvents are the result of processes so complex as to be incapable of simple chemical interpretation and detailed control. For example, the reactions that take place in destructive distillation of coal are so intricately interrelated that no one can be controlled individually, and the products are the results of the optimum conditions determined for the securing of the most abundant and valuable products. Coke, gas, and

tar are the major products, but several gallons of solvents are scrubbed from the gas from a ton of coal.

"Fine chemicals," both inorganic and organic, include those substances that result from a series of small-scale chemical operations distinguished by close attention to purity. Cost of production here is a secondary consideration. Usually a considerable number of such chemicals are made by a single plant, the production of a few days resulting in a year's supply, the same equipment being used for several products. This is in contrast to continuous production of heavy chemicals in individual and specialized equipment.

The common characteristic of all truly chemical industries is that the product is an individual substance, other substances being minor impurities. The product is used as a reagent, solvent, or ingredient in the manufacture of other products.

A few examples will make these statements more definite. Sulfuric acid is made by a series of unit chemical engineering operations carried out continuously on a large scale in equipment designed especially for this purpose. It is a typical heavy chemical, and finds use in many industries. Its manufacture is primarily a matter of applied chemistry and applied physics, and is always under the control and direction of scientifically and technically trained men. A photographic developer, on the other hand, is made in relatively small amounts. It requires the skill and care in each operation that accompany a preparation in the laboratory. The apparatus used is of such a nature that many other substances can be prepared in it with equal facility. The price is sufficiently great so that it is not necessary to take special precautions with reference to the saving of heat and power. The chief consideration is purity, and yields are of secondary importance.

A considerable number of inorganic substances occur naturally. Most of the work done in preparing them for market consists of the removal of other substances by means of unit chemical engineering operations. Any chemical changes are in the impurities, and are for the purpose of their removal.

The second class of industries includes those in which there are chemical changes, but in which most of the processes are wholly mechanical. In some cases the changes are relatively slight; in others they are profound and extensive. The main point of distinction is the physical form of the product, such as compressed gases, liquids, solutions, crystal aggregates, flakes, powders, or lumps. This form depends largely on the nature of the substance rather than on the use

to which it is to be put. On the other hand, there are many products of chemical change whose shape and physical properties are the important consideration. Articles of glass or of stoneware must have a certain form, and their chemical composition is largely a matter of the cheapest suitable materials. Portland cement is in the form of a fine powder in order that with water it may form a homogeneous paste around the grains of aggregate.

The same sugar that is in the cane and beet appears as the final product, but a series of physical and chemical changes are effected in the substances with which it is associated in order to bring about their complete removal.

The main ingredients of vegetable oils never undergo any sort of change, but the whole process of refining depends on operations and principles with which the chemist is familiar, and over which he exercises the closest control.

There are also those processes in which the main product undergoes a chemical change after it has been given a certain form. A rubber shoe or a tire has for the most part its final form before vulcanization. The composition of each part of the shoe or the tire is governed by chemical as well as physical tests, yet most of the operations of mixing the rubber with the remaining ingredients and forming them into sheets are wholly mechanical.

There are industries, now largely dependent on chemistry and chemical engineering, that until recently employed no trained chemists. Experience of centuries had shown that certain reagents and methods produced satisfactory results, but no one knew why. Chemical research revealed the basis for such changes. Science thus caught up with the art, and now chemistry has taken the lead in these industries.

Finally, there are those industries in which no recognizable or controllable chemical changes take place, but which depend to a very considerable extent on chemistry for their operation and control. Many food products reach the consumer in exactly the same chemical form as they came to the producer. Wheat is harvested, threshed, ground, the bran is removed, the resulting flour is sacked and shipped with no chemical change other than the slight effect of bleaching agents to remove a trace of color. Yet samples of this wheat were studied in the laboratory, and the selection of wheat for various uses was entirely controlled by chemical tests.

The arrangement of this book has as its basis chemical character rather than industrial use. This does not mean that use is a secondary consideration, but this arrangement is chosen for the reason that those

trained in chemistry but without industrial experience think first of chemical characteristics and then of uses and applications. The order followed is much the same as that of college texts of general inorganic and organic chemistry. It has not always been possible to adhere rigidly to this order. For example, the use of the electric current serves as a basis for grouping together a number of industrial products as varied as copper, chlorine, and graphite. However, the order, as far as possible, is based on chemical characteristics. In the field of organic chemistry, this method of grouping brings together some widely divergent industries. If the grouping had been that of use, the general topic of textiles would have included wool, silk, cotton, linen, and rayon. In this book, cotton and linen are discussed in the chapter on carbohydrates as being primarily cellulose; rayon under the same heading, as a chemical derivative of cellulose; and wool and silk, as proteins, in another chapter. In this same chapter on proteins will be found materials of such different physical properties and uses as casein, gelatin, and leather.

In general, the idea is that the reader will find the order familiar, will understand the chemistry involved in a process first, and will proceed naturally from this understanding to a comprehensive grasp of the uses of the product of this process.

In conclusion it may be said that chemistry is related to industry by setting up standards for raw materials and products; by regulating the processes of manufacture; by interpreting what takes place in every stage of manufacture; and by search for new materials, new methods, and new uses.

CHAPTER II

THE WORK OF CHEMISTS AND CHEMICAL ENGINEERS

Popular articles in newspapers and magazines have unfortunately created the general impression in the public mind that chemistry is a magical science, and have thrown around the chemist a false aura of romance and mystery. There is, of course, romance in all scientific achievement, but there is a great deal more of common sense and hard work. Relatively few people have an intelligent and well-rounded conception of what chemically trained workers do in industry.

A survey of the membership of the American Chemical Society indicates that about one-fifth of those belonging to the society are engaged in teaching. This includes most college and university teachers, and the more advanced and progressive high-school teachers. A recent study of the chemical engineering profession shows that one out of fifteen is teaching. It cannot be too strongly emphasized that progress and development in chemical industry depend to a very great extent both on thorough training of workers in the fundamentals of physics, mathematics, and chemistry, and on the experimentally observed facts and the sound reasoning based on these facts which result from research in educational institutions.

Comparatively little of such research is carried on with the direct purpose of serving a single factory or plant. For the most part, industrial research is best done in plant laboratories. Somewhat akin to university research is that done by the departments and bureaus of the United States and of some of the states. Much of this work is of more immediate and direct application than that of the universities, but it is designed to serve whole industries rather than individual plants.

A step nearer to industry are research institutions maintained partially by endowment and more largely by direct contributions of industries in the form of fellowships. The Mellon Institute of Pittsburgh is the pioneer research institute of this type in the United States. The results of the researches are the property of the donors of the fellowships, and publication of such results is restricted until

a definite time has elapsed. In more recent years a number of research organizations have been created, a considerable part of them at universities. Several trade organizations maintain research laboratories to serve whole industries, such as the canners, the meat packers, the bakers, and the cement manufacturers.

More than three-fourths of all those who are engaged in chemical work of a high grade are directly connected with industries. It is hard to draw a sharp line of distinction between the work of the chemist and the chemical engineer. Chemical engineering has been defined as "the art of manufacturing useful products through the application and control of chemical processes." A chemical engineer must be thoroughly trained in the fundamentals of chemistry as well as in physics, mathematics, and those divisions of engineering which pertain specially to his work. The chemist is primarily concerned with the sort of work that is done on a small scale in the laboratory. It is essential that the chemist should have some understanding and appreciation of engineering principles, and the chemical engineer should likewise be able to comprehend and use the results obtained in the laboratory.

The beginning of a new chemical process is in the research laboratory, and improvements of existing processes must be given their initial tests here. The work is often of a quality equal to that of the best products of a university laboratory, but differs in that it applies particularly to the materials and products of that plant. The research chemist studies the physical properties, the nature of reactions, equilibria, methods of analysis and control, all with a view to enabling the plant to make a product of high quality at the lowest possible cost. The task of the chemical engineer is to make the engineering calculations regarding quantities, yields, the handling of materials, and all factors of the flow of energy and its most efficient utilization. Successful research has in it something that results from dreaming, the creative inspiration of the artist, backed up by a great deal of hard work. Obviously the productivity of the research laboratory is not measured in terms of daily output, but is a matter that months and even years will decide.

It is an axiom of chemical engineering to "make all your mistakes on a small scale and your profits on a large scale." After the research laboratory has given all possible information, it is necessary to try the process in a development plant in what is known as "semi-works" scale. With increasing size of equipment, factors enter that could not possibly be foreseen on the basis of laboratory experience. It is neces-

sary for chemical engineers to live with a process until all these factors are understood and all difficulties are worked out. Here they gain what is often spoken of as the "know how" of the process, which no patent or laboratory report can make available. Alterations and changes in one small unit cost much less than they would in several units of factory size. Once a process has become thoroughly standardized and established, it is transferred to regular routine production on full factory scale. Most of the actual work of operation is done by what is known as "common labor." No one should make light of the skill and reliability of laborers in a chemical industry. However, most such workers have no conception of the chemical and engineering principles of the operations which they carry out. Hence supervision and direction of all parts of the industry are in the hands of chemical engineers. The operating engineer is not an experimenter. He is not blind to possible improvements, but no changes are permitted in a process until they have gone through the stages of research and development to a proved success. His results are measured by daily production, and his main concern is to keep his plant running smoothly and efficiently with the maximum output of high-grade material.

A few chemists of high grade and excellent training are needed in control work in industry, but the very large majority of analysts are routine workers. They must have certain neatness and skill and a higher order of intelligence than that of the laborers in the plant. Since the work is safe, clean, and not specially taxing physically, it attracts a certain type of labor that is satisfied with lower wages than that paid to plumbers, steam fitters, and electricians. Chemical control laboratory workers are not unionized, which has something to do with their wage scale. There is a certain type of mind and personality peculiar to an analyst, and this type finds a place in industry. Chemists are needed who can understand the principles underlying analytical procedure, and who can work out newer, simpler, and more accurate methods of chemical control. There is a continual demand for a few men who can organize and direct a staff of control chemists. There are also analysts who can do very accurate work. Such chemists are true research workers, and their abilities are accordingly recognized and rewarded. Often a process is profoundly affected by the presence of mere traces of impurities, and it is necessary to detect and estimate such materials with extreme accuracy. There appear to be two tendencies in the analytical laboratory. One is to do more very accurate work to improve the quality and uniformity of a product. The other

is to do more routine work by automatic instruments. In general, there is room for only a relatively few highly trained chemists in the analytical laboratory. At the same time, a young chemist may very advantageously spend a few months in the analytical laboratory, since there is no better place to get an intimate acquaintance with the materials and products of the plant.

There are still other phases of industry in which many more chemically trained college students could be profitably used. These are the sales, purchasing, and commercial research organizations of industries. The products of industry must be sold. The chemical industry buys vast amounts of equipment. Between the producer and the consumer there must be chemically trained salesmen and buyers. Large chemical companies employ economists with chemical training, and many financial organizations keep "chemical economists" on their staffs.

There will always be research workers who dislike and avoid executive responsibility, and whose talents and genius make it imperative that they should be well paid and retained in the laboratory. At the same time, a man capable of carrying on and directing research generally possesses qualities that make him invaluable as a business executive. Most administrative officers of chemical industries are men who understand the materials, equipment, processes, and products of their plants, as well as markets, sales, and finances.

Another group of chemically trained individuals may be described as "consultants." Included in this group are commercial analysts; experts in library research, technical writing, and patent law; and those who conduct research laboratories. Many consultants act as advisers on the basis of long and successful experience, but the tendency is rather for a consultant to maintain a laboratory with a staff of trained workers. Some consulting laboratories are devoted to commercial analyses of raw materials and products of industries not primarily chemical. Such laboratories handle a sufficient volume of business to enable them to reduce procedures to a routine and carry out a number of similar determinations at the same time. Several consulting laboratories either refuse routine work or charge such prices that only the cream of the business comes to them, and devote their energies to research and development.

A number of organizations, such as department stores, railroads, and industries not primarily chemical, employ chemists to pass on the materials which they buy, sell, or use. Such chemists are more broadly trained and more versatile than routine analysts, but are rarely of

the research type. The demand for such chemists is considerable and will increase as the use of chemistry continues to penetrate into non-chemical industries.

Summing up, these different classifications of chemically trained people connected with industry include about 80% of all those who may be said to practice the profession of chemistry.

CHAPTER III

CHEMICAL ORGANIZATIONS

Chemical organizations are of two kinds, the determining factors being training and interest. Those that make a certain amount of training and experience prerequisites of membership are in the main composed of specialized groups; those that are founded on common and general interests are larger, and include in their membership most of those who belong to the former type of organization.

The American Institute of Chemical Engineers resembles several other engineering societies in that a certain amount of training and experience must characterize each of its members. For senior membership, ten years' experience as a chemical engineer are required, with allowance for time spent in graduate work. There are also junior and associate members. This organization meets twice each year, and in addition to hearing technical addresses and papers and joining in social meetings, makes inspection trips to chemical industries. The papers presented at the meetings are collected and printed in book form.

The Electrochemical Society has much the same general policy as to meetings and publication of its proceedings. The field covered by this organization is quite a broad one, since electrochemistry finds application in the most varied industries.

There are a number of organizations to which chemists belong by virtue of their special interests. For example, the American Society of Testing Materials numbers many chemists among its membership; there is an Association of Official and Agricultural Chemists; those interested in the paper industry belong to the Technical Association of Pulp and Paper Industries; and there are many others that attract chemists.

There are New York sections of two of the larger*foreign chemical societies: the Society of Chemical Industry, which is primarily an English organization, but which has more than once had an American president; and the Société Chimie Industrielle of France.

The American Institute of Chemists admits to its organization only those who have had certain training and experience, either as fellows or associates, and strives to maintain certain professional and ethical standards by the combined efforts of its members.

CHAPTER IV

SOURCES OF INFORMATION FOR CHEMISTS AND CHEMICAL ENGINEERS

There are in the United States and Canada about eighty important chemical libraries, in which may be found a relatively complete collection of books and journals. In general, a chemical library is rated on its collection of journals. No research worker can stop with a book, however modern; it is necessary to go to the original articles describing previous work in the field. A large number of less complete libraries possess a few sets of journals. Of the eighty larger libraries, about one-half are in universities, and the remainder are fairly evenly distributed among government bureaus, public libraries, clubs, institutes, associations, and companies. Among several valuable books on the use of chemical literature, Mellon's "Chemical Publications" and Crane and Patterson's "A Guide to Chemical Literature" deserve special mention.

In his book "Introduction to Organic Research," Professor E. Emmett Reid has this comment on reading the literature of chemistry:

To be sure the research chemist spends a large part of his time searching the literature for things that bear directly on his own problem, and necessarily so, but he cannot afford so to narrow himself as to see one small segment of chemistry. The man of one idea has not a whole idea, for his one idea is incomplete without its relation to other ideas: the zenith is related to the whole horizon. One must read broadly of many things in order to think deeply on one thing. The research chemist must read everything about his own field, but can not afford to neglect the rest of chemical literature. It is remarkable how much light is thrown upon a problem from distant sources: one can hardly read a piece of investigation of any sort without finding something that suggests an idea about his own problem. *

It is possible to do a great deal of excellent industrial research with only a few sets of journals, provided that these include the important American journals, and particularly *Chemical Abstracts*. Even small libraries should have the British publication, *Chemistry*

* Quoted by permission of D. Van Nostrand Co.

and Industry, formerly known as the *Journal of the Society of Chemical Industry*. Prior to the foundation of *Chemical Abstracts*, readers of chemical literature were dependent upon *British Chemical Abstracts*, the *Journal of the Society of Chemical Industry*, and the German *Chemisches Zentralblatt*. Inexpensive photoprints of articles outside these journals can be obtained from large libraries.

The individual chemist in industry, by virtue of his membership in chemical organizations, receives each year a considerable number of journals. In addition to these, one publication is widely used by the chemical profession in this country, *Chemical and Metallurgical Engineering*. It is devoted largely to the publication of technical news of the chemical and chemical engineering developments in industry, economic reviews, markets and prices, book reviews, notes on plant equipment, patents, personal notes, editorials, and general articles of varied nature on all fields of chemical engineering and industrial chemistry. Occasionally a whole issue will be devoted to a single topic, this being particularly true of the January issue each year, which deals entirely with the progress and economic status of all important chemical industries.

The *Journal of Chemical Education*, though primarily for students and teachers of chemistry, contains a surprising amount of valuable technical and industrial information, particularly for those who are unfamiliar with a field and wish a clear general discussion of the subject.

There are numerous technical publications devoted to particular fields of industry, and also publications concerned with the business side of the chemical industry, including prices, markets, and trade conditions. Among these are *Chemical Markets*; *Oil, Paint and Drug Reporter*; and the English publication, *The Chemical Trade Journal and Chemical Engineer*. It is obviously impossible to read several journals completely and entirely. The up-to-date chemist keeps generally informed as to the progress of the science, reads editorial comment that reflects current chemical opinion, follows the news that pertains to chemical industry, and then devotes his attention largely to his field and specialty. Any intensive work on a problem demands a thorough review of the literature on the subject in collections of journals that are found only in chemical libraries.

Few realize that the United States Government is the largest scientific publishing concern in the world. The publications of the Bureau of Mines, the Bureau of Standards, the Bureau of Chemistry of the Department of Agriculture, and the U. S. Geological Survey are of

special interest to the chemical industry. Those working in food industries follow the bulletins of the Public Health Service. The business side of chemistry is very closely associated with the Tariff Commission, the Bureau of Foreign and Domestic Commerce, and occasionally with documents covering the hearings and investigations of Congressional committees. Lists of government publications are available from the office of the Superintendent of Documents, from which all publications may be bought at very low cost. Technical journals usually list new government publications.

A number of universities, technical schools, and also state experiment stations issue bulletins covering research done by them, which are in general very useful. Various research institutions have regular publications. Surveys of progress in chemical industry are published under the auspices of the National Research Council, and an English publication of a similar nature is sponsored by the Society of Chemical Industry of London. The National Research Council has also published a volume with two supplements, known as "Bibliography of Bibliographies on Chemistry and Chemical Technology."

A patent on a chemical process contains very little discussion of data or principles, but sets forth the claims of the inventor or patentee concerning the equipment and methods used. A full knowledge of all patents bearing on a certain phase of chemical industry is necessary on the part of those who plan developments and improvements. United States patents may be obtained directly from the Patent Office, and also photoprints of foreign patents. The *United States Patent Gazette* is a most useful publication, and other countries have similar publications. Chemical patents are listed and often briefly abstracted in *Chemical Abstracts*.

Modern advertising in the chemical industry is a most valuable and accurate source of information. Propaganda has largely given way to facts. Many manufacturing concerns issue data sheets, tables of constants, and descriptive bulletins of very high order. A collection of catalogues and bulletins is of great value. The advertising pages of technical journals give information that compares very favorably with that gained from the reading matter between the advertising sections. The *Chemical Engineering Catalog* contains hundreds of pages of advertising material of manufacturers of chemical and chemical engineering equipment, announcements of practically all modern books on chemistry and chemical technology, and a series of most valuable indexes of practically every type of apparatus and chemical used in industry.

Books that are encyclopedic in their nature, such as Thorpe's "Dictionary of Applied Chemistry," Watt's "Dictionary of Chemistry," and Ullmann's "Enzyklopaedie der technischen Chemie," are found in every large chemical library. The technical chemist continually uses such sources as Mellor's "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Gmelin's "Handbuch der anorganischen Chemie," Richter's "Lexikon der Kohlenstoffverbindungen," and Beilstein's "Handbuch der organischen Chemie." These sets are brought up to date periodically and are essential in all library work. The International Critical Tables are very largely distributed, not only in libraries but also among private collections. Practically all chemists continually use such pocket handbooks as the "Handbook of Chemistry and Physics" and Van Nostrand's "Chemical Annual." Commercial chemicals are listed together with all necessary information for their industrial use, in the "Condensed Chemical Dictionary."

The American Chemical Society, through a group of editors and advisers, has sponsored a series of monographs, part of which are technological in their nature, in order to encourage the writing of necessary books by authors best fitted by training and experience to discuss the subjects. Most technical chemists are limited to the purchase of a few books, either for themselves or for their companies, and must exercise very careful judgment in selection. In this their best guides are the impartial and thorough book reviews to be found in *Chemical and Metallurgical Engineering* and in *Industrial and Engineering Chemistry*. Many journal articles contain fairly complete bibliographies listing the more important books as well as journal references, and books often refer to other books on the same topic. Those who read journals closely, and particularly who attend chemical society meetings, become acquainted with the men who are doing the best work in their fields, and buy books on the basis of the reputation of the author.

In addition to chemical society meetings, expositions are held, at intervals, which are largely attended by those interested in the chemical industry. Such expositions are of three classes. They may be general in their nature, such as those held in the last few decades in Chicago, St. Louis, San Francisco, Jamestown, and Philadelphia. Secondly, there are expositions that pertain to industries with which chemistry is intimately connected, such as the Oil Industries Exposition and the Power Show. There is finally the Chemical Industries Exposition, held every two years in New York City. This exposition is devoted to showing chemical engineering equipment, raw materials,

products of chemical industries, laboratory apparatus and supplies, books and periodicals, and the work of trade organizations and government bureaus. In order to add still further to the educational value of such an exposition, a series of lectures for students is given at each exposition, the speakers being men who are recognized authorities in their fields of chemical industry.

CHAPTER V

ANALYTICAL CONTROL IN CHEMICAL INDUSTRY

Chemical industry depends at every stage from raw material to finished product on analytical control. Many non-chemical industries employ analytical chemical control in purchasing materials and in evaluating their products. An important use of chemical analysis in many industries is in "trouble shooting." This involves finding out by means of chemical analyses the cause of failure of some product or manufactured article. Many large wholesale concerns require frequent chemical analyses. Such analyses not only regulate the price paid for materials and products and determine the usefulness of substances, but they also give information concerning the operating efficiency of equipment. Cities, states, and the United States Government employ many analytical chemists to test water, food, and all manner of materials.

Students of analytical chemistry must learn principles and procedure by slow and painstaking repetition, the emphasis being on fundamentals. Few institutions have time or place in analytical courses for instrumental and electrometric methods. With this background the student who first makes contact with a routine industrial control laboratory is surprised by the lack of thorough chemical training on the part of the workers in the laboratory, and even more so by the unbelievable number of determinations made by a single worker in a day.

For a routine control method to be a success it must be short and uninvolved, unmistakable in its physical changes, and capable of accurate results in the hands of the average manipulator. In the larger laboratories every step has been carefully worked out and standardized, and each worker is limited to a relatively few kinds of determinations. Equipment is also standardized, and the number of samples handled at a single "run" is determined on the basis of the greatest efficiency. Every motion is repeated so many times that great speed and a very high degree of precision are attained.

Whenever possible, gravimetric methods are avoided, and volumetric, photometric, or electrometric methods are substituted. Com-

paratively few determinations require more weighings than that of the sample taken. The most rapid type of balance available is used. Balanced watch glasses, counterpoised dishes, and the use of factor weights characterize industrial analyses. For example, weights of sample are so chosen that the weight of the final precipitate can be recorded, with proper shift of decimal point, as the percentage of the element or compound being determined, or the burette reading can represent the percentage directly.

At this point it is necessary to distinguish between "accuracy" and "precision," two terms which are often used interchangeably but which have different meanings. "Accuracy" has been aptly defined as "constant deviation from the truth," and "precision" as "probable limits of deviation from truth, due to uncontrollable factors operating in a random manner." If a method constantly gives deviations of 0.5% from the true value, it would be said to be 0.5% accurate. It would further be necessary to indicate whether the deviation was greater or less than the true value, that is whether the degree of accuracy was +0.5% or -0.5%. On the other hand, the precision of a method would be said to be $\pm 0.5\%$ if "successive, identical samples analyzed by the method, using reasonable care and skill, will on the average deviate from one another by 0.5%." Rapid methods are standardized by the use of longer and more involved procedures of unquestioned precision. The standardization of an analytical method involves the analysis of a sufficient number of aliquots of known composition to justify the application of statistical treatment to the data. From this is deduced the precision, or probable error of the method. It is often not necessary that a method for testing a product in its intermediate stages be of extreme precision. The limits of allowable error must be determined, and methods chosen that will fall within those limits and still give maximum possible speed. A referee method must not only be very precise, but must be repeated several times and often by more than one analyst. A very high grade of research work is necessary to develop methods of detection and estimation of substances, particularly in a new process. If the industry does research, the analyst must constantly aid the research worker by telling him the composition of new materials. The estimation of organic compounds depends also on such factors as solubility, melting point, cooling curves, and similar physical phenomena.

Certain procedures, called "field" methods, are adapted for use entirely outside a standard laboratory. Determinations of the approximate amount of iron and hydrogen ion concentration by means

of color comparison disks, of alkalinity by titration with tablets containing an acid salt, sulfates by a candle photometer, and alcohol by boiling point are illustrations of the meaning of this term.

The expression "trace" is in bad repute because of its indefiniteness; yet such a small amount that it may be regarded as a "trace" may be sufficient to condemn a product. In testing food products, state and government laboratories often report only the presence or absence of a forbidden substance. If the precision of the method is known, the expression "trace" can and should be replaced by "less than a specified amount." There are many methods capable of surprising precision by which very small amounts of some substances may be determined. Practically all such tests depend on the production of a definite color and shade.

The majority of analyses of substances with which chemical industry is concerned fall in the classification of "partial analyses." Frequently it is not necessary to know the complete composition of a material. The nature of insoluble material is often not important, and it is only necessary to know the amount and composition of the soluble substances. It is only necessary to test boiler feed water and the contents of the boiler for certain ions, usually not more than a half dozen at most. It should not be taken for granted, of course, that only those components present in largest proportions are important. Very small amounts of some substances are in some cases decidedly injurious to the product, and it is quite necessary to know how much is present and in what form.

Certain analytical methods are known as "proximate methods"; they are arbitrary and empirical tests by which very complicated materials may be compared and standardized. The best-known tests of this nature are those universally used in the evaluation of coal. (See "Power Plant Chemistry.") These tests do not give the exact amount of a pure substance, but they are reasonably accurate, easily reproducible, and of great value in judging the quality of a coal in comparison with other coals of known performance record. Somewhat of the same nature are the "accelerated corrosion tests," which have some application in evaluating materials of construction. Such tests must be calibrated against actual, long-time field tests.

It is obvious that the majority of operations in analytical chemistry depend on physical properties, but it is necessary to distinguish between those in which chemical changes take place and those wholly physical in their nature. Many tests in chemical industry involve no chemical change, such as tests for viscosity, specific gravity, refractive

index, and degree of rotation of polarized light. The introduction of such physical methods as fractional crystallization, cooling curves, phase rule equilibria diagrams, and the like, has made possible the evaluation of numerous products that defied ordinary chemical control methods.

Many instruments have been devised for use in a particular industry or with a certain type of product. The nitrogen content of many explosives in which the nitrogen is present in pentavalent form as inorganic nitrates or nitric acid esters is determined in a "nitrometer," in which the volume of nitric oxide obtained by decomposition of the sample measures directly the percentage of nitrogen present. Too much stress cannot be laid on instrumental methods in chemical analysis. For many years the chemist has depended on the microscope, and such pioneers as Chamot have devised special microscopical analytical methods. The metallurgist depends largely on his photomicrographs in the study of alloys. In recent years the X-ray has become of great importance in the testing laboratory. Practically every industry has a set of instruments peculiar to that industry. Also certain types of apparatus have rather wide application.

Certain methods, called "official," are the result of cooperative study and research on the part of chemists representing an industry quite generally all over the country. Such methods are worked out under the auspices of some technical organization, which adopts them as official after sufficient trial and investigation. The organization that has most to do with official recognition of commercial and industrial analytical methods is the American Society of Testing Materials. Committees of this organization, often cooperating with committees from technical societies, make a thorough study of the precision and reproducibility as well as simplicity of a method. When adequate evidence has been accumulated, a procedure is tentatively adopted, and after a further period of trial it becomes an "official" method. In the field of agricultural products and materials used by this industry, the methods are made official by adoption by the Association of Official Agricultural Chemists. There are a number of standard books on analytical methods, and it is customary to refer to the books from which the methods were taken if no official methods are available.

In recent years there has been a very decided trend not only towards the use of instrumental methods, but also towards methods that are essentially automatic in their nature. For a long time, engineers have judged performance of boilers by automatic equipment, which determines and records the carbon dioxide and carbon monoxide in stack gases. The determination of hydrogen ion concentrations,

commonly known as pH values, is very generally accomplished by the use of organic indicators. Many materials, however, are of such nature that the indicator method is not satisfactory, and electrometric methods are very generally employed, these depending either on conductivity of solutions or on the electromotive forces of a standard half cell used with the unknown material in the other half cell, which contains a hydrogen electrode or an oxidation-reduction indicator like quinhydrone. The number of industries that depend on an accurate and continuous knowledge of hydrogen ion concentration is most impressive. Although in many cases determinations at intervals are satisfactory, there is an increasing demand for the use of apparatus that will give a continuous record of results, and at the same time automatically regulate valves and controls to insure uniformity of conditions. A recording potentiometer with automatic temperature compensating devices may control valves or tilting weirs so that the correct amount of a solution is continuously added in a process. Only very slight electrical impulses are necessary with the modern appliances developed by the radio industry to carry such control of large-scale equipment. The photoelectric cell is a most valuable aid in such procedures. Any method that depends on development of turbidity or change of color of a solution may be used with a photoelectric cell to actuate recording and controlling machinery, the intensity of light passing through the solution governing the entire process. A somewhat similar method is used for continuous determination of mercury vapor in the air, paper sensitized with sulfide solution darkening by the formation of mercuric sulfide and cutting down the light received by such a cell. The heat developed by catalytic oxidation of carbon monoxide to carbon dioxide is used in connection with sensitive thermocouples and recording potentiometers in determining the amount of carbon monoxide in vehicular tunnels.

It is not desirable to be too optimistic at present as to the possibility of automatic devices replacing routine chemical workers. A very large part of analytical control for many years to come will likely be done by skilled labor, but many operations now depending on the taking of samples in the plant, making tests in the laboratory, and reporting back to the plant operator will be conducted by automatic control devices located in the plant as a part of the apparatus used in the operation. At the same time more attention will be paid to methods of great precision used for the estimation of small amounts of materials not hitherto regarded as significant, the work being done by highly trained chemists, fully capable of interpreting and understanding their results.

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Within the present century the process of hydrogenation has put on the market vast amounts of hardened vegetable oils, which have essentially the same characteristics and properties as hog lard. The packing industry, which makes lard, has not suffered, because the advance in the demand for all shortenings has increased so much that their markets have grown in spite of the fact that around half a million pounds of hardened oils are sold annually. The butter industry has withstood the competition of oleomargarine of all sorts, partly on the merits of butter itself, and partly on the political influence of the dairying industry in securing restrictive legislation.

The price of leather has been influenced very largely by the competition of rubber and coated fabrics, which are put to the same uses. Yet the price of a pair of shoes has very little relation to the cost of the leather from which they are made. Since hides are a by-product of the packing industry, and the number of animals slaughtered depends very largely on the demand for meat products, there would be a shortage of leather if it were not for such substitutes. At the same time, these substitutes serve to keep down the price of hides to a point at which there is very little profit to the stock raiser.

The story is told of a man who developed an excellent acid blue dye at a time when such dyes were scarce, and found, after his plant was built and running and the product had been put on the market, that perspiration turned the blue to a vivid red. It is thus important to learn all the properties of a product before deciding that it will revolutionize an industry and make its manufacturers wealthy. Some day, some one will write a great book on "Chemical Processes That Have Failed," which will be more instructive than descriptions of many processes that have succeeded.

In the field of textiles, rayon, a fiber resembling silk but made by chemical processes from wood pulp or cotton linters, is now more extensively used than silk, and may in time have a very decided influence on the cotton industry. At the same time, the demand for such fabrics has grown so fast that the silk industry has not as yet been seriously injured, but rather helped by the competition.

This sort of thing does not always take place. The history of the collapse and almost total disappearance of the natural indigo industry because of the superior quality and cheaper price of synthetic indigo is well known. Wood distillation is suffering from a series of attacks which are the results of intensive research in widely varied fields. The demand for wood charcoal is much less because of the development of processes for making with coke what is known as "charcoal iron."

The newer solvents have divided the market with the solvents made from wood-distillation products, but the heaviest blow to this industry was synthetic methanol from high-pressure catalytic treatment of water-gas products, which controls the market once occupied by "wood alcohol." Since fully 80% of all methanol goes either into the production of formaldehyde for synthetic resin manufacture or into alcohol denaturants, this is a large and quite stable market.

The chemical industry has the advantage of great flexibility. Haynes has pointed out that the clothing manufacturer knows exactly how much cloth is required for each garment, and the bolt maker knows to a fraction of an ounce how much steel rod will be required for a thousand bolts. The amount of a chemical product from a given raw material, however, may be subject to a great variation. By virtue of the great demand for gasoline, the petroleum refiner has supplemented physical methods of separation of hydrocarbons by chemical methods of decomposition of higher hydrocarbons by heat and pressure, and is even now experimenting with converting all the crude petroleum to gasoline by high-pressure hydrogenation. At the same time, the development of high-compression internal-combustion engines has greatly increased the demand for gasolines made by cracking processes that have high "anti-knock" ratings. When there was no demand for light oils and tars, and a limited demand for gas, the beehive oven was the only economic method of producing coke, and gas was made in the small horizontal retort. The by-product coke oven is now not only used to make coke, but all the other products are caught and used, and this type of oven is being rapidly adopted by the public service corporations for making domestic and industrial gas.

The hazards of chemical industry from the standpoint of fire, explosion, and injury to the health of employees are great. Until comparatively recent years no insurance company would accept as a risk any plant manufacturing chemicals. Investigation showed that scientific control constituted a very appreciable protection, and that chemical industries were not by any means impossible risks. Leading insurance companies began to employ chemical engineers, whose duty it was to investigate plants and processes from the standpoint of fire, explosion, and employer's liability. With the point of view of safety uppermost they were able, in cooperation with companies whom they served, to reduce materially or remove altogether what were once thought to be inevitable conditions. One of the greatest sources of danger in chemical processes handling inflammable or explosive materials is that of static electricity. Sublimation of such substances as naphthalene,

anthracene, and anthraquinone will generate considerable quantities of electricity by friction of solid particles; this is also true in many widely diverse industries, and in some where danger is least suspected. The handling of gasoline is particularly dangerous unless precautions are taken to ground all trucks by means of dragging chains. Intelligent cooperation with safety engineers and physiological chemists has cut down very greatly the health hazards of chemical industry. With the safeguards of knowledge and care, the risks of chemical industries have been lowered, but the danger is still relatively high because of the properties of the substances handled, a great many being toxic, corrosive, or combustible.

Probably in no other type of industry is the relative cost of development of a process so high as in the chemical industry. Laboratory research is regarded as very expensive, but the chief cost is that of salaries, probably half of the amount spent for salaries constituting laboratory and overhead charges. The cost of that sort of research is quite small in comparison with the money required to bring the process from the laboratory to large-scale production. Assuming that the product is of proved marketability, it is essential that every step in its development should be sound and thorough, and no step should be taken until everything that should precede it has been successfully completed. The idea must be mechanically and chemically sound, and its reliability must have been proved beyond question in the laboratory. Every piece of data that has any bearing on the process must have been collected and systematically arranged, and an impressive and reliable body of knowledge amassed before a process is ready to graduate from what may be called the "beaker stage." Redman has pointed out that the time when a process has been thoroughly proved a success in the laboratory is just the time when it begins to cost a great deal of money. It is rare that any process can be transferred directly from the laboratory to large scale at once. The stages of development vary according to the nature of the process and product, but the maximum number necessary is considered to include the "small sized model," the "large sized unit," the "small commercial plant," and finally the "commercial plant." In each of these, difficulties must be ironed out, defects remedied, and valuable information gained. Every step is increasingly expensive, and if the process is one of any considerable magnitude, a great deal of capital is required, and the project should be undertaken only by a company of such size and financial standing that a complete failure and abandonment of the process would not be felt as a great financial shock. The exact cost of every

part of a process, even those parts that are normally regarded as entirely similar to other processes, must be known. The whole project must be viewed in a calm, dispassionate, and critical way, which is a very hard thing for the enthusiastic inventor or promoter to do. It is here that the outside consultant is valuable. It is possible to live so long in such close proximity to a process that the point of view is distorted and perspective is lost. The chemist and the engineer must share with the cost accountant, the sales executive, the market expert, and the financial executive the responsibility for a process. It requires a most reliable product that can be sold at a good profit to offset the very great cost of process development.

The economic value of real scientific research has been discussed so much that one might be accused of being a "zealous exponent of the obvious" who attempted to say anything more. It is now very definitely recognized that the only real and lasting progress that has been made in the chemical industry has been by those companies that included research in their program. At the same time, so much has been said that the investing public has gotten a twisted view of research, as if it were something magical, and something that paid immediate and very large dividends. Some chemists have undertaken elaborate programs of research that had little bearing on the problems of their industry, with the result that research was discredited by business men as an expensive luxury. In spite of mistakes on the part of the public and the chemical profession, on the whole, research in chemical industry has been sane, thorough, and fundamental, and has paid exceedingly well as an investment.

The location of a chemical plant is governed by a number of factors whose importance varies with the particular industry. Tyler sums up these factors thus:

1. Source of Raw Materials. Price at source, cost of buying, transportation costs, reserves, and adequacy and permanency of supply are all essential considerations. Obviously these are most important for industries concerned with very large quantities of relatively low-priced products such as portland cement, on which the margin of profit is small. Water is not only necessary in production of power, but is often a raw material, and must be free from anything that would injure the product or interfere with the process.

2. Market for Products. Market radius depends on the bulk and value of the product. Coal can be shipped long distances, but the gas made from it must be consumed within a very small radius, else all profits vanish. Natural gas is piped long distances, but is extremely

cheap at the wells and has about twice the heat value of manufactured gas. Products that involve unusual shipping hazards encourage highly localized production. On the other hand, high-priced products such as pharmaceuticals and dyes may be shipped great distances, if other factors are more favorable.

3. Sources of Fuels and Power. In general, this is not a controlling factor in location except for the electrochemical industry, which must have cheap electrical power. Some other industries require a great deal of fuel for process heating in such unit operations as evaporation, drying, and fusion.

4. Source of Labor. Chemical industries require intelligent labor, but continuous processes and automatic control mean that the amount of labor is relatively small, and very little is skilled manual labor such as is required in many mechanical industries. Hence proximity to large labor markets is not highly essential.

5. Transportation Facilities. This is also a matter of bulk. It is a noteworthy fact that the majority of chemical industries, except where local needs and markets dominate, are on waterways, where both rail and water transportation are available.

6. Economic Relation to Other Industries. Many chemical industries are very undesirable neighbors, owing to fumes and wastes. Sometimes these may be profitably caught, but as a rule most waste-treatment plants are installed to avoid litigation. Hence isolated regions are often most desirable. A plant may be located at one place to use the wastes or products of another plant. There are also factors of labor sources and "educated" banking facilities, which draw like industries together.

7. Capital Requirements. The cost of unimproved land as contrasted with property that has gas, water, sewage, and power connections, the cost of building, local regulations, and the attitude of the community or state with reference to taxation are factors that may be included as capital requirements.

In 1928 a series of articles covering the whole United States by certain definite geographical divisions was published by *Chemical and Metallurgical Engineering*, which served to give a clear picture of the present status, the resources, and the possibilities of chemical industries from the standpoint of plant location.

The design of a plant is a fundamental chemical engineering problem. All other factors being equal, an intelligently and carefully designed plant has every advantage over one that has grown up in a

hit-or-miss fashion by alterations and additions. This is largely a matter of storage and of flow of materials in manufacturing, assuming that the actual processes are of the highest possible efficiency. Also the problem of future expansion must be provided for.

"Accounting and Cost Finding for the Chemical Industries" is the title of a recent book by George A. Prochazka, Jr. The following summary of important considerations in this field is largely based on the conclusions of this book. It is essential that any chemical industry be able to account continually and accurately for all costs of production just as it accounts for costs of advertising, marketing, and administration. The "job cost" method generally used in the mechanical industries is applicable also to processes that are conducted by the batch, and to finding costs with a series of batches; it is the method which should be used in these cases. Continuous operations do not lend themselves to this method, and here it is necessary to use what is known as the "process cost" method. With this as a general accounting control method, detailed costs of each unit operation can be worked out, so that a plant may not only know the cost per ton for processing its raw materials, but also what each operation, such as grinding, crystallizing, drying, and the like, costs per ton of product. A single factory will probably use all methods, since some operations are batch and others continuous.

Costs should be obtained on a departmental basis, so that each service rendered can be accurately evaluated. In this way a worthwhile picture of the costs of manufacture can be obtained, and quick and intelligent comparisons can be made with competing selling prices. Much of what is called overhead is really capitalized labor. Whatever plan of cost accounting is used, every effort should be made to arrive at departmental costs, so that the various physical operations involved in the manufacture and associated with them can be added to the cost of the direct materials as definite accomplishments requiring particular expenditures for depreciation, taxes, insurance, expenses, supplies, wages, and salaries.

Fluctuations in yields and variations in rate of production are apt to make unit costs unintelligible unless the numerous constant costs are reduced to unit values on a standard basis. It is often necessary to have several standards to meet the needs of several rates of production. Actual costs cannot be taken except for such long periods of time as a year. The use of standard costs makes the accounting work so much simpler and gives a figure that is so much more serviceable

that of late years there has been a pronounced trend toward the use of this method. It is absolutely essential at all times to compare an actual cost with a standard of performance.

The organization of a chemical industry does not differ from that of other industries except in the emphasis on research and chemical training on the part of business executives. A chemical industry will have purchasing, sales, transportation, finance, construction, operating, research, personnel, and statistical departments. In charge of all operations is a technical director, and in larger companies there are directors of such divisions as control, research, and development. At the present time, most successful chemical industries have as their financial and business executives men who received the training of a chemist or a chemical engineer rather than that included in the ordinary business administration courses. The sales division must be largely composed of technically trained men, not necessarily by long experience in the plant, but certainly by sufficient contact with processes to understand them and the application of their products to the uses of the buyer.

The whole matter of waste disposal is one of sound business principles and an accurate, unprejudiced, and thorough analysis of costs, markets, and profits. Chemical economists are often inclined to regard the utilization of wastes as necessary only when a nuisance is to be avoided, or where there is a clear profit to be realized. There have been many tragic failures in business because of unorganized and intermittent efforts to make a profit out of a waste. If the waste is a nuisance to a community or to another industry and must be treated in some way to avoid legal action, the cost of its treatment is a normal and reasonable charge against operation, and anything that can be recovered and sold is regarded as merely lessening the cost of disposal and not as a source of profit.

On the other hand, there are instances of treatment of wastes that have shown sufficient profit to draw a company into another industry and convert them into large producers. A company producing metals from sulfide ores was faced with suits from agriculturists because of the devastating effects of sulfur dioxide fumes. Consequently these fumes were converted into sulfuric acid. Since sulfuric acid presented certain difficulties in transportation, and phosphate rock was near at hand, great quantities of phosphate fertilizers were made as a means of disposing of the acid. So profitable was this business that the same company in more isolated regions, where fumes would not have caused legal action, made acid and phosphate fertilizers, and thus became

leading producers in a field they were originally forced to enter purely to avoid damage suits. The alcohol industry absorbs the waste molasses of the sugar mill. The beginning of the cottonseed oil industry was an effort to avoid the nuisance of the accumulation of the seeds, which were regarded by the textile industry as worthless. For many years sulfur and particularly chlorine were made from the waste calcium and hydrochloric acid of the Leblanc process for sodium carbonate, and it was only when cheaper sources of these materials were developed that the Leblanc process gave way to another. There may be a complete change in the demands of other industries, so that a waste may become the main product. Before the days of internal-combustion engines the low-boiling hydrocarbons from petroleum were wastes. They could not have been safely or profitably stored for the use of later generations, and the only sane and economic disposal of them was to burn them.

Closely akin to the disposal of trade wastes at a profit is the question of conservation of resources. Here too there has been a great deal of general and sometimes sentimental talk and a dearth of facts. A note of sound common sense was struck by Teeple when he showed that a relatively small number of elements are necessary to human existence, such as carbon, hydrogen, oxygen, nitrogen, sulfur, phosphorus, calcium, magnesium, potassium, sodium, and a few others, and that these are relatively abundant. When any other material begins to get scarce, its price goes up, its use diminishes, and research finds something else to take its place. Wood was once thought to be indispensable to humanity. Now it is no longer needed as a fuel, as a structural material, or as a source of furniture, and with the development of synthetic methods and the utilization of farm-grown fibrous materials, it is not even necessary for making solvents, paper, or fabrics. However, a survey made by Rommel indicates that the rapid growth of wood on the Atlantic seaboard in the southern states insures against any shortage in the supply of wood as a fibrous material. Teeple points out furthermore that the chemist is gradually removing the source of friction between nations, since "the real service of the chemist lies in the fact that he is freeing or rendering us more and more independent of any specific raw material to supply any specific want."

All this does not mean that squandering of natural resources should be encouraged as a policy, but that conservation must pay dividends as it goes. A great many improvements in processes, largely in the way of heat recovery and elimination of unnecessary handling of

material, have contributed greatly to conservation, particularly of fuel and power. Modern factory chimneys are much less prone to spread black smoke and soot all over the neighborhood, with consequent damage to property and public health running into millions yearly for any large city, since modern methods of combustion, based on principles of physics and chemistry, mean complete utilization of the carbon which was once lost up the chimney. Centralization of heating and power plants, a better handling of the problem of distribution of fuels and power, and the substitution of continuous for batch methods of operation have all resulted in great economic gain.

No industry has attracted the attention of the public in the matter of waste, conservation, and possibility of immediate exhaustion of resources as much as the petroleum industry. For years the public has been told that in less than a decade all the petroleum in the United States would disappear, and that the end of the world's supply was in sight before the close of the century. It is also known that there has often been overproduction, and that the consequent low prices have done little to encourage economical methods of making those commodities derived from petroleum. In spite of this, there is no industry in which greater progress has been made from the standpoint of engineering efficiency and complete utilization of energy. A vast amount of work still remains for the chemist in finding out what can be made from petroleum as a raw material. The present demand is predominately for motor fuel; the industry is meeting that demand by pressure distillation, and is experimenting on a large scale with hydrogenation. In 1925 a comprehensive report of a committee of the Board of Directors of the American Petroleum Institute was published in which the whole field of supply and demand in the United States was thoroughly reviewed. All the resources of this great industry were used in making this report, since it represented the combined efforts of a large number of operators, economic and statistical experts, engineers, geologists, physicists, and chemists. This report is not only a model for other industries, but represents the greatest single cooperative economic study that has ever been undertaken by any industry. Its scope may be better understood when it is remembered that the petroleum industry employs three-quarters of a million people, and includes an investment of about nine billion dollars.

One of the most interesting problems affecting chemical industry and one that has come in for a great deal of public attention is that of the utilization of the great nitrogen fixation plant at Muscle Shoals, Alabama, which was built by the United States government during

the World War to produce ammonium nitrate as a military explosive. This plant was erected under tremendous pressure in a few months, and cost around \$60,000,000. This does not represent its real value, since time was of primary importance and was paid for liberally. The plant, however well constructed originally, is now hopelessly obsolete and is no longer essential either in national defense or fertilizer production. This great chemical factory has been visualized by the agricultural industry as a source of cheap fertilizer. Economists who have had chemical training are generally agreed that the Muscle Shoals plant has very little bearing on the production of cheap fertilizer. The issue is clouded by the question of power as well as by various political issues. The available power has been popularly overestimated; the average horsepower available is less than 200,000, and the often-cited production figure of 600,000 is a practical impossibility. The Muscle Shoals plant is capable of producing 40,000 tons per year of fixed nitrogen in the usual terms of total nitrogen, and for several years was regarded as a valuable supplementary source of military explosives. The great developments in the manufacture of synthetic ammonia have so changed the situation that this plant is not now needed. Military requirements in a major conflict would not be over 150,000 tons of fixed nitrogen, and the present synthetic ammonia capacity in the United States is 320,000 tons of nitrogen.

Both private and governmental agencies have for several years been making a detailed study of foreign trade in chemical products. In general, imports are considerably in excess of exports, the ratio being from 1.60 : 1.00 to as low as 1.47 : 1.00. Imports are mainly such natural monopolies as potash from Europe, vegetable oils from the tropics, nitrates from Chile, camphor from Japan, and some tar oils which are not profitably produced in this country. The leading articles of export are ammonium sulfate, phosphate rock, caustic soda, light oils from coal gas, rosin, and some dyes.

The relation of the chemical industry to other forms of manufacturing is such that it is a matter of international concern. There is not only the question of natural monopolies on the part of certain nations, but also that of centralization of industries within those nations whose resources and whose labor and business conditions make such industries particularly suited to them. Most of the readily available supplies of potassium salts are within the boundaries of Germany and France. After the experience of being cut off from such supplies during the World War, the United States is making considerable progress in a search for potash deposits within her borders that will com-

pare in extent and importance with the European resources. Because of the development of nitrogen fixation no nation is any longer dependent upon Chilean nitrate for fertilizers. The fact that practically all military explosives are made by the use of nitric acid has led several nations to heavy governmental subsidies for their nitrogen fixation industries. An attempt by the British to keep up the price of rubber because of the financial difficulties of rubber growers, the bulk of all plantations being within the British empire, led to the planting of a large acreage by American capitalists in Liberia on the western coast of Africa, and subsequent abandonment by the British of all efforts to fix the price by governmental methods. Chemical economists are inclined to regard artificial methods of regulating prices by tariffs, subsidies, and restrictions as transitory, and in the long run not only useless but harmful.

Differences between nations in their attitude towards combinations of industries often result in discrimination against those nations which restrict such combinations. In Germany, combinations of capital in numerous industries are not only not restricted, but are even encouraged and supported by the government. In very recent years there have been several international combinations in Europe that have enormous potentialities. There is, of course, the possibility of such combinations breaking down from their own weight and from international jealousies and disagreements. In the United States, monopolies are closely regulated by the government, and every effort is made to avoid them. The laws governing monopolies were made under entirely different trade conditions, and before transportation and communication had so greatly lessened the size of the world from an economic standpoint. The history of modern business has very clearly shown that monopolies which have attempted to gain complete control of a commodity or an industry with a view to fixing exorbitant prices have always failed. There is a very distinct difference between co-operation and monopoly. The future has often been rendered extremely unsafe for a small concern because of the rapid shift in methods, uses, and demands, and because of ability of large concerns to preempt markets. Industries that are in the hands of large corporations are able to absorb changes, develop and put into use new processes, pay off the costs by an increase in price, and then lower the price to increase sales, at the same time making increased profits because of the great volume of business. On the other hand, research is apt to thrive more and cost less in small concerns where there are men who have a real contribution to make. Research in very large

concerns has often been too costly because of the unwieldy nature of any large organization and the difficulty of fixing individual responsibility.

Howe proposes that these five things be done. Industries must have better organizations within the limits of our present laws. There must be more business chemists on the directorates of companies. Research of all sorts must be better supported, and there must be a better supply of men trained to do research. Government agencies should be expanded to permit more information concerning manufacturing and business to be gathered by technically trained men. Foreign loans should be more carefully examined and more conservatively made to avoid ultimate harm to American industry.

The history of the synthetic organic dye industry in the United States is one which illustrates the general nature of the problem of international relations. Up to 1914 the United States imported most of such dyestuffs in finished form; with the exception of one or two small and struggling concerns, the dyes made in America were merely assembled from German intermediates. The magnitude of the business was not sufficient to interest American capital. The making of dyes requires a proportionately large staff of highly trained chemists, engineers, and operatives. The system of German cartels was such that competition in America could be promptly crushed and the market held by cutting prices of German dyes below their cost. Textile plants largely had German master dyers, who naturally preferred and specified German dyes. So the matter stood when the World War began. For the first time the American public realized our helplessness. The value of the dyes themselves was relatively small, but several major industries depended on them. At the same time it was realized that a kindred industry, also small, the manufacture of synthetic pharmaceuticals, was practically non-existent in this country, and our supplies of necessary remedies had been cut off. There was a great deal of feverish activity and unsound development, with the result that some very poor products appeared on the market. However, several large companies undertook the problem on a most thoroughly sound basis. German patents, never worked in this country but merely serving to prevent American manufacture, were seized as alien property. As sources of information they were of little value. All the methods and processes had to be worked out by laboratory and plant research at great cost. Each of three great companies spent considerably more than a million dollars before they were able to produce their first pound of indigo for the market. Within four years the dye industry

in the United States was on as sound a chemical and engineering basis as the one Germany had spent more than fifty years in developing, but the cost had been tremendous, and the industry was faced with enormous loss if left without tariff protection until a readjustment of conditions. Fortunately such protection was afforded, first by an embargo against German dyes, and then by a tariff. After a few years the industry was on its feet, with an excellent technique, experienced management, a sound research program, and well-developed markets on the basis of high quality and reliability of products. At the same time, the wage scale in Germany has risen by virtue of the increased power of labor to demand and secure a just share of profits. This shift of economic conditions has put this industry in a position to compete on a fair and equitable basis with the foreign industry, so that it is on a par with other industries, and enjoys only such tariff protection as is in keeping with the common national policy.

Although, as former Assistant Attorney-General Donovan has shown, our system of competition (equal opportunity, individual initiative, freedom from governmental regulation, absence of power to control prices or allocate territories or customers) is contrary to that of many foreign nations, there is nothing in our laws to prevent cooperation between similar industries in research, development of methods, and sharing information; nor is it contrary to our laws for industries to combine for export business in order to reduce selling costs, to purchase raw materials collectively, to bring about standardization, and to eliminate "cut-throat competition" on the part of foreign nations. It should also be remembered that the same laws that apply to American owned business, governing combinations in restraint of trade, also apply to foreign companies seeking to do business in America. These provisions of the Wilson Act of 1894 were invoked as recently as 1925, and upheld by the United States Supreme Court in

After all is said and done, nothing can take the place of business brains, technical skill, specialized and usable knowledge, and advancement based on a sound and progressive program of research.

CHAPTER VII

UNIT OPERATIONS AND EQUIPMENT

Chemical industries are very closely interrelated because of the similarity of the operations carried on in them. The products of two industries may differ widely in properties and uses, and at the same time the industries may be very much alike in apparatus and methods. Every chemical industry may be regarded as being made up of a succession of "unit chemical engineering operations." The number of such operations is relatively small, and not all industries employ all of them. The chemical engineer has due regard for the chemical nature of the substances with which he deals and the chemical changes taking place in them, but at the same time devotes most of his attention to such factors as handling of materials, the application of heat, the mechanical strength and chemical resistivity of materials of construction, and such typical operations as disintegration, mechanical and phase change separation, and mixing.

It is not the purpose of this book to discuss the fundamental laws and principles upon which unit operations are based. This chapter is written in order to give a general idea of what unit operations are and in what sort of equipment they are carried out. It will not be possible to go into details or to describe all kinds of equipment, but the more important operations are discussed and a few typical pieces of equipment are illustrated.

1. MATERIALS HANDLING

The first consideration in any chemical plant is the handling of materials. This is particularly true where the materials are cheap and bulky and the margin of profit is small. Older chemical plants often merely grew up, but modern plants are designed on the basis of the simplest, most efficient, and least expensive method of transporting materials.

Solids. Material that is composed of lumps, or lumps and fines, is often handled by the grab bucket. The most common variety, known as the "clam-shell bucket," consists of two hinged segments that are

pulled apart and dropped on the pile of material. The edges of each segment dig into the solids, and when the bucket is pulled up the two portions unite and serve to hold the contents until opened for discharge. The bucket may be handled by a locomotive crane, by a monorail with hoisting and control cables, or by a traveling crane, which gives both width and distance of operation.

Continuous conveyors are used to a great extent in standardized operations where distances are not excessive. Ordinary belting run-

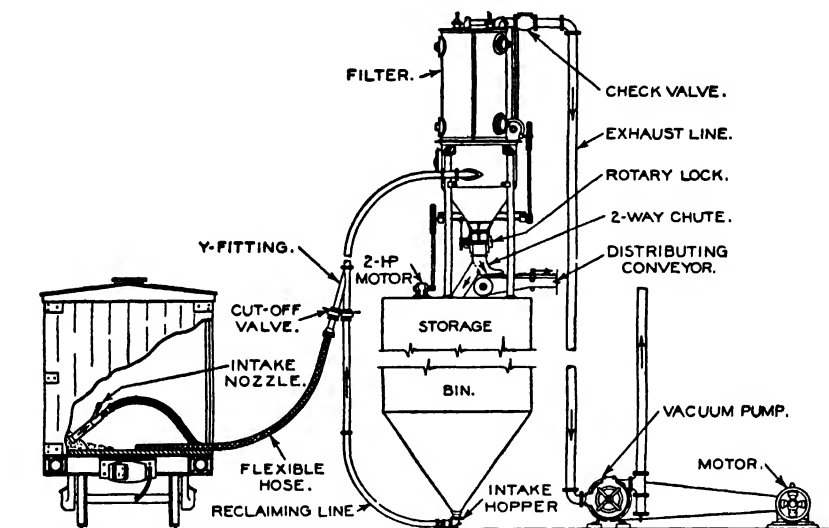


FIG. 1.—Draco Pneumatic Conveyor. Courtesy Rust Recovery and Conveying Company, Cleveland, Ohio.

ning on rollers constitutes the simplest type. If the angle of repose of the material is low, the belt may run over a set of rollers to give it a cross-section of a shallow U. Instead of a continuous belt of leather, coated fabric, or steel, series of linked plates constitute the apron or platform conveyor. For many uses the plates are replaced by V-shaped buckets. If the buckets are free to swing they require a tipping device at the point of unloading, but if they are rigidly held they can convey material only in a vertical direction. Packaged materials are advantageously conveyed by gravity on sets of rollers, which are either in a straight line or in a spiral setting.

A trough in which link belts or parallel chains drag a series of scrapers, known as "flights," is a somewhat simpler conveyor than a bucket elevator. Instead of flights, a spiral blade on a shaft constitutes a continuous flight and is the common screw conveyor.

Finely divided solids are handled in currents of air with the same ease as gases. Even a mixture of fines and lumps, where the largest material does not exceed 2 in. in diameter, may be handled by powerful air currents through pipes. The air serves to cushion the walls, and there is very little shock of impact even at bends. Dust is caught in bag filters before the air passes to the vacuum pump.

Liquids. Piston pumps for handling liquids depend on forcing the liquid into a compartment, automatically preventing it from returning

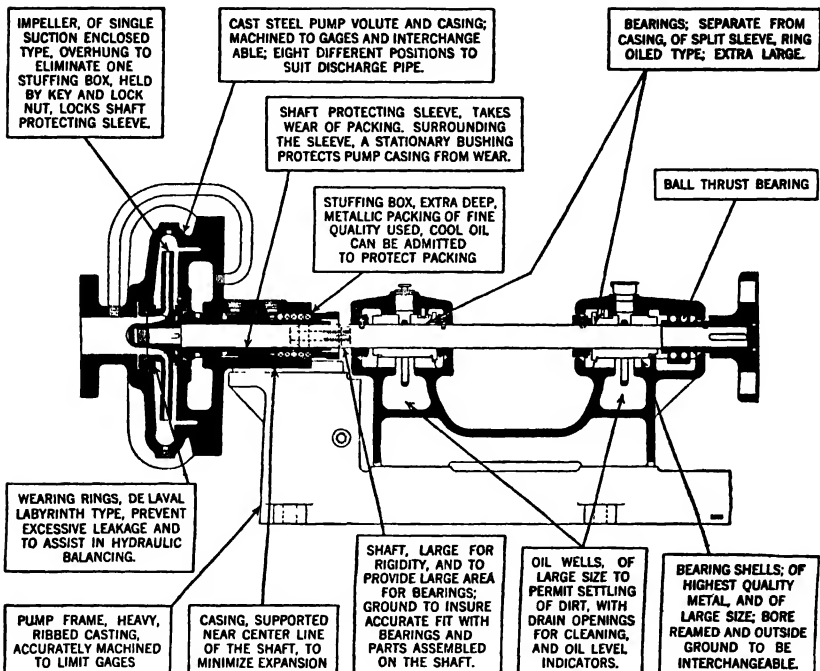


FIG. 2.—DeLaval Centrifugal Pump. Courtesy DeLaval Steam Turbine Company, Trenton, N. J.

by means of valves, and forcing it on its way, a valve opening to permit discharge. Centrifugal pumps are continuous and unidirectional in their action, and depend on feeding the liquid into a compartment within which a rotor or impeller is moving at a high rate of speed. The liquid is given a rotary motion and flies off the rotor when the first opening is reached. Recent developments in materials of construction have greatly extended the usefulness of centrifugal pumps.

Air is often used in handling liquids, particularly those that are highly corrosive. A liquid may be lifted to a height that is less than

its barometric height by removing the air above the liquid by means of a pump. For relatively short elevations, air lifts are often used. These depend on forcing air in near the bottom of a J-shaped pipe so that the weight of the liquid in the short leg will lift the relatively light mixture of air and liquid in the longer pipe. A pipe which is set in a well containing liquid and into which air is admitted towards the bottom of the well functions in the same way. Molten sulfur is lifted in this way as much as 2500 ft., the air being under heavy pressure.

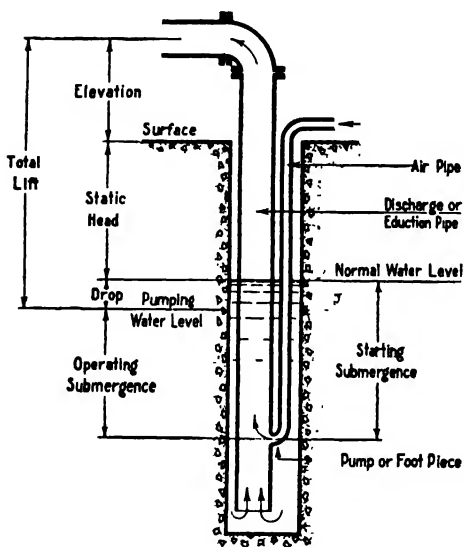


FIG. 3.—Air Lift. Courtesy Schutte and Koerting, Philadelphia, Pa.

Liquids in a closed container may be expelled by the use of compressed air. The ordinary "acid egg," also called "blow case," or "montejus," is essentially a container equipped with a delivery pipe, a discharge pipe reaching to the bottom, and an air pipe. If operated by hand the container is filled and the filling line valve is closed. Air is admitted and the liquid is forced up into the discharge line. When all liquid has been expelled, the excess air escapes through the same line. Such equipment may be operated automatically by the use of float and check valves.

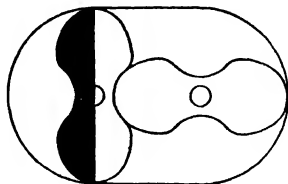
Efficiencies of acid eggs are

low, and they are not used when any other kind of equipment can be substituted.

Gases. When high pressures are desired, gases are handled by piston or plunger type pumps. Gases at relatively low pressures are moved by continuously revolving impellers. These may be simple blades, as in the ordinary fan type of blower. Two impellers, each of figure 8 form, rotating in opposite directions in an elliptical casing, make up the cycloidal blower. As will be shown later, such blowers also serve as gas meters. The Nash Hytor pump functions either as a blower or vacuum pump. It is made up of an elliptical casing with two inlet and two discharge ports, and in this casing is a rotor in the form of a circular casting equipped with a series of blades. The pump

is partly filled with liquid. Twice in each revolution the liquid forces gas out of the pump, and twice the liquid is thrown to the walls to create a partial vacuum and draw gas into the pump.

Measurement and Storage of Materials. Batches of solids and liquids may be weighed by means of hopper, platform, or tank scales.



CROSS-SECTION SHOWING METHOD OF DETERMINING DISPLACEMENT OF THE CONNERSVILLE BLOWER

IMPELLERS ARE FORMED OF TRUE MATHEMATICAL CURVES THAT FOLLOW A WELL ESTABLISHED EQUATION AND DISPLACEMENT CAN BE ACCURATELY DETERMINED

TIMING GEARS INDICATED BY BROKEN LINES ARE ACCURATELY MACHINED AND RUN IN OIL

SHAFTS ARE OF STEEL AND ARE PRESSED INTO IMPELLERS. EITHER SHAFT MAY BE EXTENDED TO RECEIVE DRIVE.

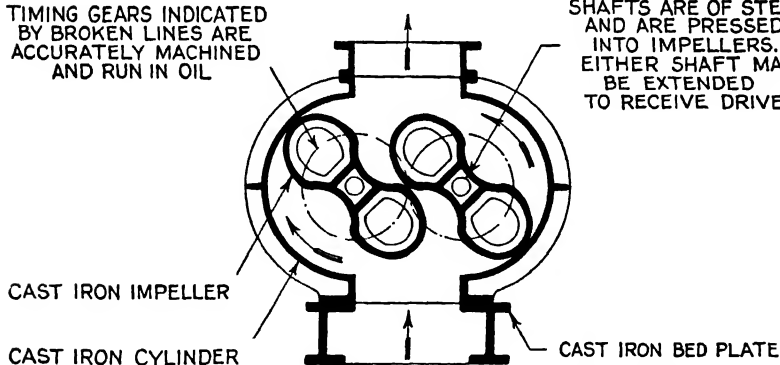


FIG. 4.—Cycloidal Blower. Courtesy The Roots-Connersville-Wilbraham Blower Company, Connersville, Ind.

Continuous weighing and measuring devices for solids and liquids are necessary in many industries in order to get accurate proportioning of materials that are to be mixed. One device for proportioning consists of a hopper with a bottom valve connected to a balanced roller over which a belt conveyor passes. If too much material is fed to the conveyor, the roller is depressed and the hopper discharge opening is restricted. In the same way a deficiency in feed allows the counter-

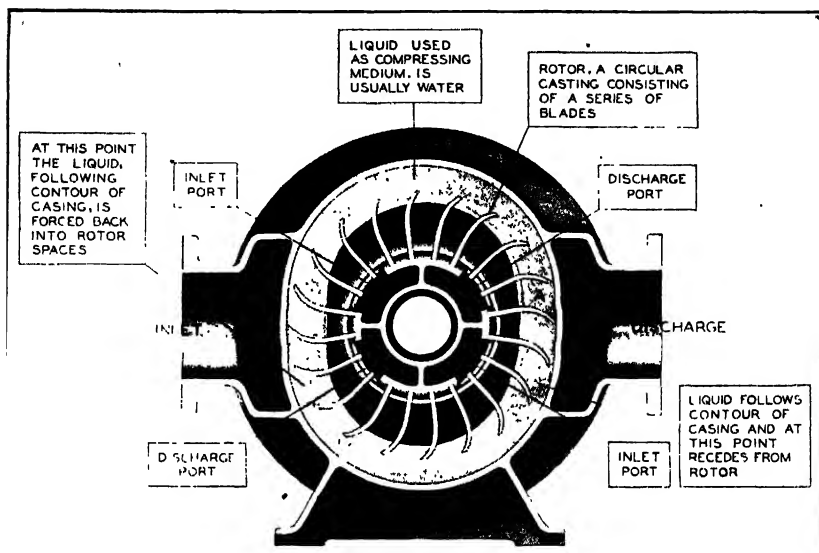


FIG. 5.—Nash Hytor Pump. (Cross section.) Courtesy Nash Engineering Company, South Norwalk, Conn.

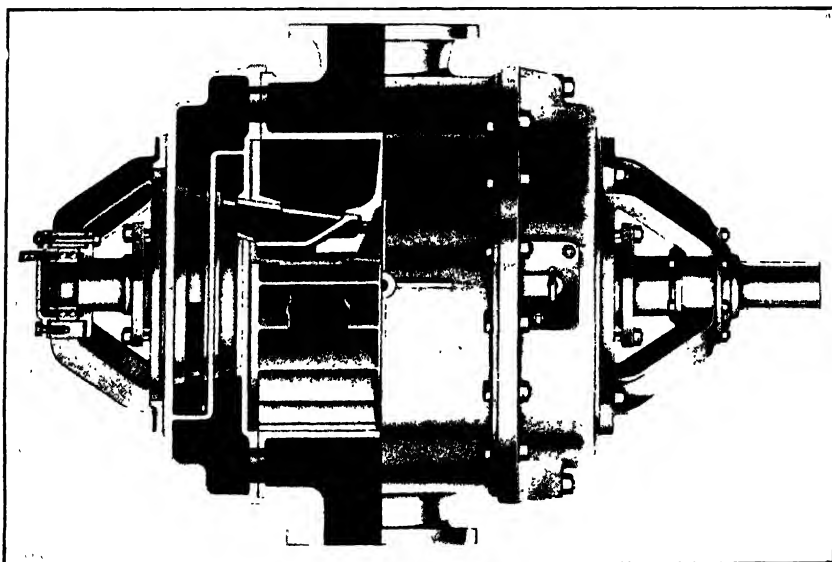


FIG. 6.—Nash Hytor Pump. (Viewed from top with part of casing cut away to show impeller and ports.) Courtesy Nash Engineering Company, South Norwalk, Conn.

balanced weight to lift the pulley and open the hopper valve. The relative position of roller and weight may also regulate the flow of liquids that are to be mixed with solids.

Both gases and liquids, commonly classed together as "fluids," can be measured with a fair degree of accuracy by the difference in pressure set up on opposite sides of an orifice in a pipe or a constriction of special shape. The latter device is commonly known as a "Venturi" meter. The difference in pressure may be measured by observing the differences in the heights of two liquid columns connected to opposite sides of the orifice or constriction; by the quantity of electric current flowing through conductors of increasing length, the number immersed in mercury depending on pressure variations (Republic meter); or by the effect of differences in pressure on a bell inverted in a sealing liquid (Bailey meter). The movement of a series of vanes in a flowing liquid may be used as a means of measuring the quantity of the liquid.

Since the displacement of a cycloidal blower can be very accurately determined, these blowers are efficient gas-measuring devices. When gas of reasonably uniform composition and therefore of constant specific heat is involved, a precise method of measurement is to heat the moving gas in an insulated section of the pipe through an exact interval of temperature (2° Fahrenheit, for example) and to measure and record continuously by integrating devices the exact quantity of electrical energy required by the heating elements (Thomas meter). The ordinary household meter employs a pair of bellows and operates dry. The wet type of gas meter, which varies in size from a small 0.1 cu. ft. test meter to very large station meters, is a horizontal cylinder in which a sectional drum revolves. By maintaining a standard and uniform level of liquid within the meter, a definite quantity of gas is collected in each section of the drum, sealed by the liquid, and delivered to the discharge opening. The number of revolutions of the drum thus records the quantity of gas handled.

Gases that are used in relatively small quantities are commonly compressed and stored in cylinders. Those gases that do not liquefy under pressures up to 1800 lb. at room temperature can be handled only in small quantities. Manufactured gas made from coal or coke is stored in holders that provide for fluctuations in demand upon a continuous and unvarying supply. The older type of gas holder is essentially a cylindrical tank containing water in which is suspended a cylinder closed at the top and open at the bottom, around which are a series of concentric rings. The upper edge of each ring is bent over outward and downward, and the lower edge inward and upward,

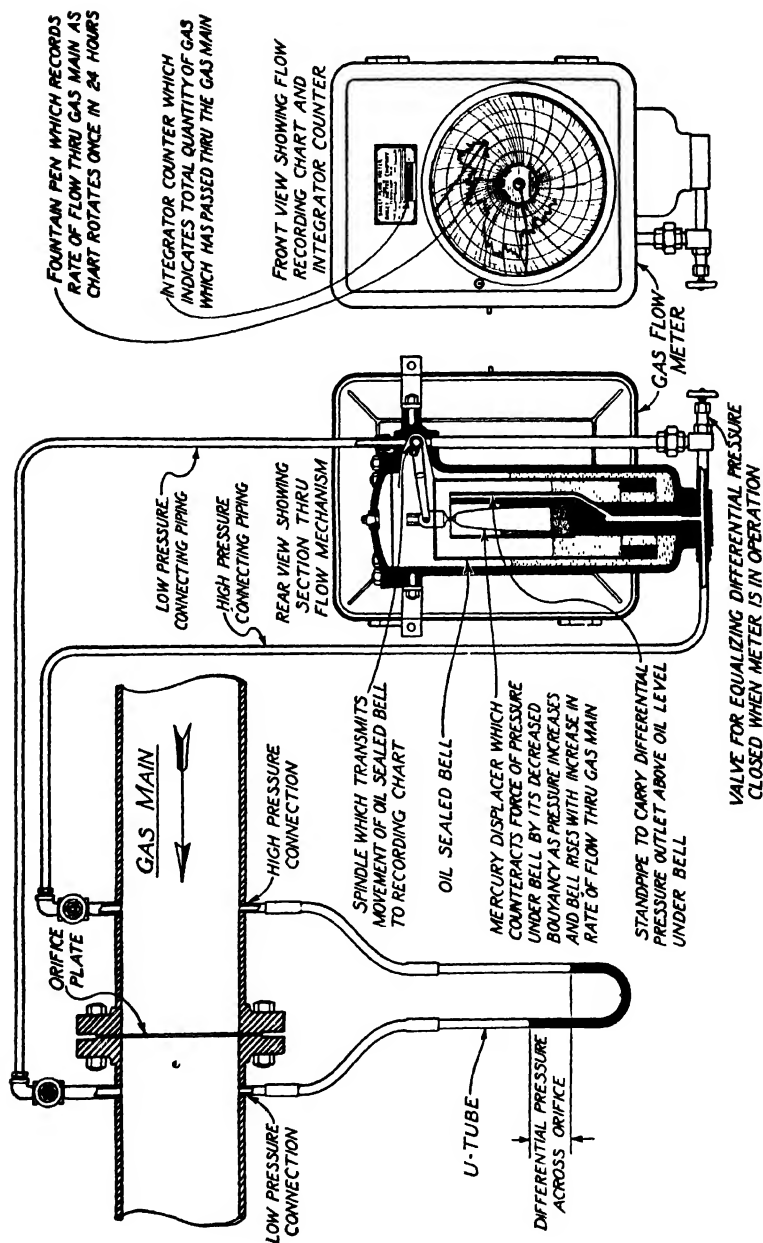


Fig. 7.—Bailey Meter. Courtesy Bailey Meter Company, Cleveland, Ohio.

while the lower edge of the inverted cylinder has the same arrangement as that of each ring. As gas is fed into the holder the cylinder or bell rises and pulls up one after another of the rings until it reaches the limit of its capacity. A series of heavily braced posts serve as vertical tracks for wheels attached to the top of the holder, and thus the rise and fall of the telescopic bell are vertical and uniform.

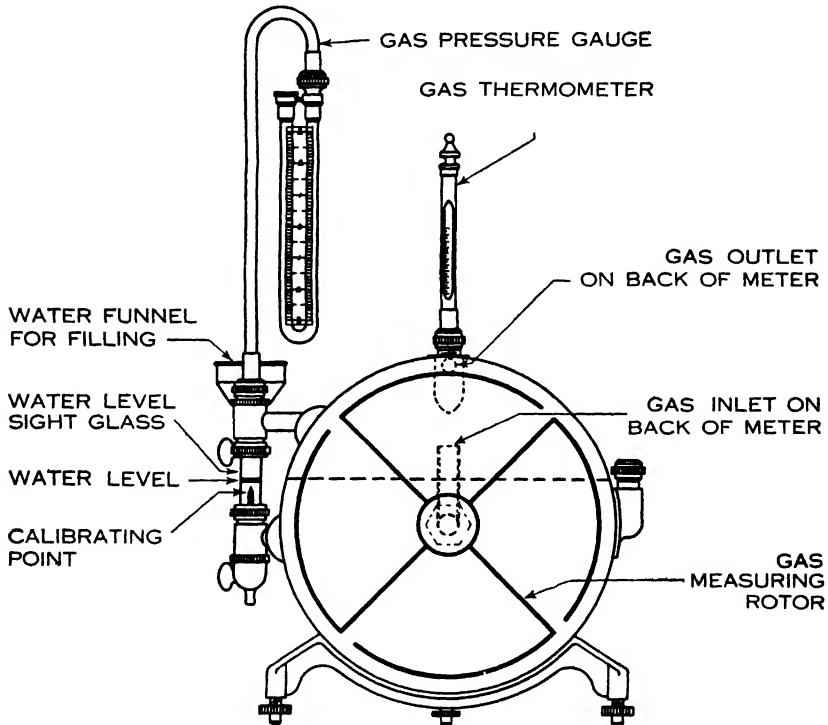


FIG. 8.—Sargent Wet Test Meter. Courtesy Precision Scientific Company, Chicago, Ill.

A more modern storage system is the "waterless gas holder." This is essentially a vertical cylinder in which there is a closely fitting piston, which rises and falls as gas is introduced and withdrawn. The holder has a heavily braced roof equipped with skylights and ventilator, but there is no gas between the floating piston and the roof. Tar serves to lubricate and seal the piston. The tar is distributed evenly over the walls, and also forms a liquid seal in a "tar cup," which extends around the outer edge of the piston. The tar is collected at the bottom of the holder and is returned to the top.

2. HEAT AND COLD APPLICATION

The flow of heat energy from a higher to a lower level is by conduction, in which the molecules are in relatively fixed positions with reference to each other; by convection, in which masses of molecules vibrating at a greater degree of intensity move into an area of lower temperature; and by radiation, which involves electromagnetic waves

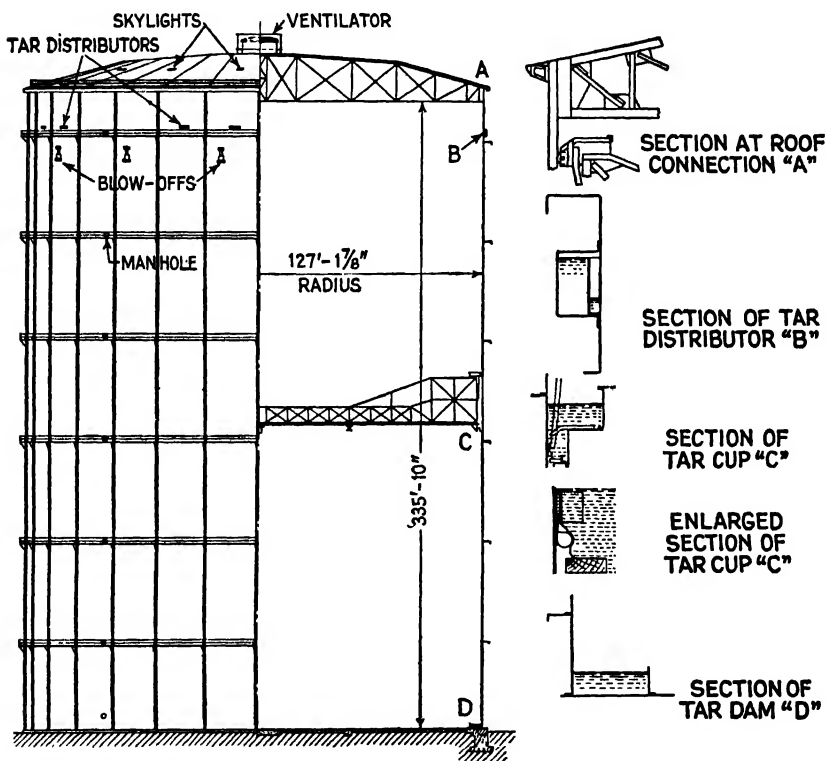


FIG. 9.—Waterless Gas Holder. Courtesy The Bartlett Hayward Company.
Baltimore, Md.

obeying the same general laws as those of light. The flow of heat through gaseous and liquid films is solely by conduction, and film effects are quite large and costly. A very thin film of a fluid may offer as great resistance to the flow of heat as a considerable thickness of a solid. The film effect is greater for gases than for liquids. The higher the velocity of the fluid, the thinner is the film and the smaller its effect, but it is never possible to get away entirely from fluid films.

Heating Methods and Equipment. The most common method of transferring heat in the chemical industry is by means of condensing steam. In addition to the sensible heat of the vapor itself there is the much larger quantity of heat resulting from condensation. Higher temperatures are attained by superheated steam, but the difficulty of handling a vapor under pressure limits its use. High-boiling organic compounds such as diphenyl, diphenyl oxide, and hydrocarbon oils have some use as carriers of heat, and lead and mercury are also employed. The use of mercury as a liquid should not be confused with its use in vapor form in the production of power.

Hot gases are very extensively employed to transfer heat. In some cases they may come in direct contact with the materials to be heated, but where there are objections such as contamination or dilution of products, the heat is transferred through the walls of a container or duct. Fuel gases may be burned in direct contact with the material to be heated, as in glass tanks, furnaces, and kilns.

Electrical heat is expensive even at the cheapest current rates, but has the advantage of close regulation as well as convenience, cleanliness, maintenance of good working conditions, and ease of control and regulation.

Since the total radiant energy per unit surface is proportional to the fourth power of the temperature, radiant heat is employed in many cases. Gases burn much more readily on the surface of hot solids, and these incandescent solids radiate heat.

Equipment for the production of heat is extremely varied and will be described later in connection with a number of processes. Any hot material that is allowed to cool without giving back its heat to the process represents that much waste. Hot liquids and gases may be caused to give up a part of their heat to other, cooler fluids through the walls of the ducts through which they flow. The heat of condensation of vapors is used to preheat liquids that are to be evaporated or distilled. Gases may be preheated by being passed over the surface of hot solids. Air and fuel gases are often preheated before they are mixed and burned.

If the hot products of combustion are continuously passed through thin-walled ducts, which in turn give their heat to the entering air and gas, the method is referred to as "recuperative." In the "regenerative" method the hot furnace gases pass over firebrick laid in such a way that the maximum possible surface is exposed. The large masses of refractory material become quite hot and serve as a reservoir of heat. After an interval the hot gases are deflected to another set of

chambers or regenerators containing cooler refractories, and the cold air and cold fuel gas are passed separately through the previously heated regenerators. In the meantime the exit gases are now heating up the brick in the regenerators through which they pass. After an interval the flow is reversed and the air and gas enter over the very hot brick, while the hot furnace gases restore the temperature of the brick that have been cooled by the entrance of cold gases. The amount of temperature fluctuation in any one spot in a regenerator is rarely over 200° F., and the masses of firebrick remain continuously quite hot. Regenerative heat exchange is illustrated in the discussion of glass, metallurgy, and coal products. Gases escaping from both recuperative and regenerative systems still contain considerable heat, and may serve to evaporate and concentrate solutions or to generate steam in low-pressure waste-heat boilers.

Refrigeration. The same general principles of heat transfer apply to the lowering of temperatures and the removal of heat. It is entirely a question of the reference temperature. If water supplies are used that are the temperature of the atmosphere or the ground from which they are drawn, the operation is regarded as cooling; but if lower temperatures are attained, either directly or indirectly, by the use of evaporating liquids of low boiling point, the operation is called refrigeration.

Heat is very commonly removed by the circulation of water whose freezing point has been greatly lowered by the addition of considerable quantities of sodium or calcium chloride. The brine in turn has lost its heat by being brought into thermal contact with a rapidly evaporating liquid of low boiling point such as methyl chloride, sulfur dioxide, or most commonly anhydrous ammonia. The vapors of these liquids are condensed by means of compression and cooling, and the liquids enter the cycle again.

Cooling brines are handled in coils, in jackets, and in double pipe chillers with the brine in the outer annular space and the material to be chilled in the inner pipe. Solid carbon dioxide has a limited use as a refrigerant, being commonly packed around the material that must be kept cold. In certain operations, such as diazotization reactions in making azo dyes, great quantities of ice are added to the reaction mixture.

3. DISINTEGRATION

The reduction in size of solids and dispersion of solids in liquids and of liquids in other immiscible liquids may be considered together

under the broad general head of disintegration. The reduction of large fragments to somewhat smaller size is known as crushing; reduction of the latter to a coarse granular mass may be spoken of as grinding. The production of a very fine powder from a coarse material is called pulverizing. There are no sharp lines of division between these operations. In both crushing and grinding some fine material is produced.

Crushing and Grinding. A jaw crusher is made up of a heavy hopper on one side of which is the fixed crushing surface and on the opposite side is a movable jaw, pivoted either at top or at bottom and caused alternately to advance and recede by means of an eccentric, a

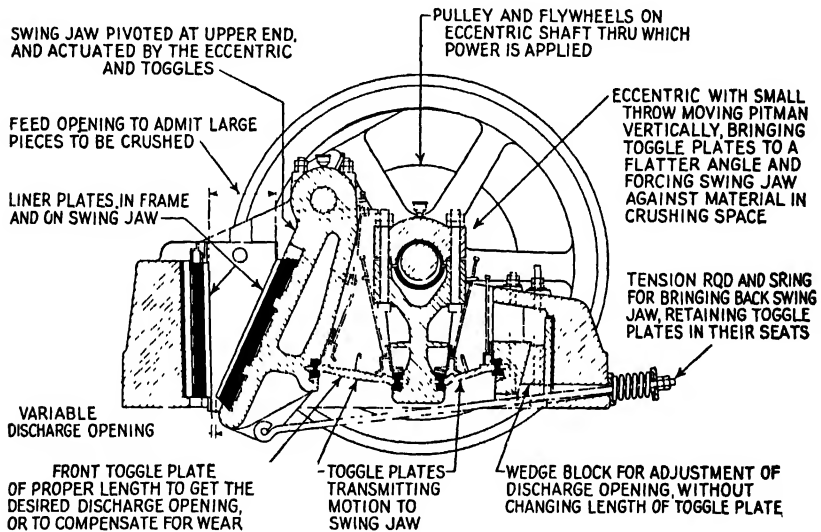


FIG. 10.—Jaw Crusher. Courtesy Allis-Chalmers Manufacturing Company, Milwaukee, Wis.

pitman, and toggle plates. Jaws pivoted at the top are more commonly used. If material of very high crushing strength accidentally falls between the jaws, bolts in one of the toggle plates will shear and allow the object to fall through without serious damage to the crusher. Such crushers vary all the way from laboratory models operating on 1- or 2-in. material up to giant machines handling lumps the size of an office desk. The jaws are ordinarily corrugated in order to give the effect of suspending a fragment between two points of support and applying a force between the two.

A gyratory crusher consists essentially of a hopper of circular cross section, usually corrugated, within which a heavy cone set in an

eccentric bearing is made to gyrate. Since the slopes of the cone and the hopper are opposite in direction, the material gradually works down and ultimately escapes through a variable opening between the largest part of the cone and the smallest part of the hopper. The distance between a fixed point of the hopper and an opposite point on the cone continually shifts so that a lump is alternately squeezed, broken, and released. The eccentricity of the bearing which operates the cone is slight, being not more than 2 in. in a crusher 20 ft. high. The

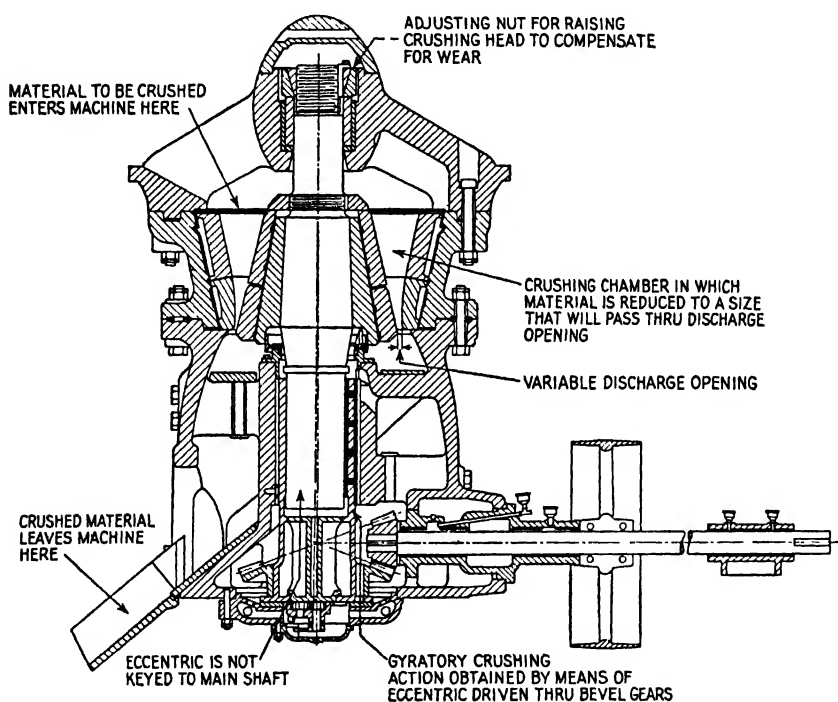


FIG. 11.—Gyratory Crusher. Courtesy Allis-Chalmers Manufacturing Company, Milwaukee, Wis.

cone is supported at the top by a loosely fitting bearing attached by a spider to the hopper. The eccentric bearing is driven by bevel gears. The cone is free to turn but does not rotate to any extent. The top of a gyratory crusher is often set into the floor of a bin of ore or rock. Unlike jaw crushers, a gyratory crusher is very hard to choke.

The modern cone crusher operates on somewhat the same principle but differs in a number of important respects including: a feed plate on the cone shaft; much greater eccentricity in the bearing and hence

wider gyration; greater speeds; different shape of crushing cavity in the way of a long parallel zone; and complete support of the gyrating cone at the bottom. An additional feature is a series of springs that allow the bowl to rise and release non-crushable material.

Crushing rolls catch the object and force it between them with consequent reduction in particle size, the rolls being held close together by powerful springs. The space between the rolls determines the size of product. The bearings of the rolls are such that they can pivot

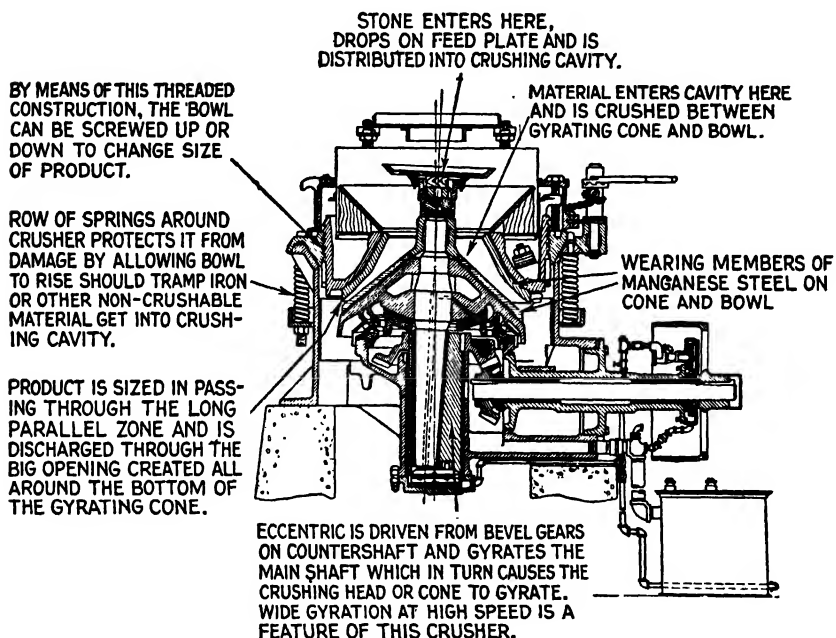


FIG. 12.—Symons Cone Crusher. Courtesy Nordberg Manufacturing Company, New York City.

slightly to permit a piece of “tramp” iron to escape between the rolls against the force of the springs. Whether a lump will be drawn through or will merely ride on the rolls depends on the relative size of the lump and the rolls. The angle formed by the tangents to the circle of each roll at the points touching the lump must be below a certain value (never exceeding 50°) known as the “maximum angle of nip.”

Breaking solids by impact is the underlying principle of the hammer mill. The material to be broken is dropped into the path of rapidly moving hammers, and is broken as the result of blows. In most such mills the hammers are pivoted on rotating disks. When the

hammers and material travel in the same direction the mills are classified as under-running. This type is more common than the over-running mill in which the hammers move in an opposite direction to the feed, and in which the fragments resulting from the lump being struck in mid-air are driven against anvil plates for further disintegration. The lower part of a hammer mill is made up of heavy screens. A series of plain and shredder rings held on the parallel shafts of a rotor constitute a special type of hammer mill. When the rotor

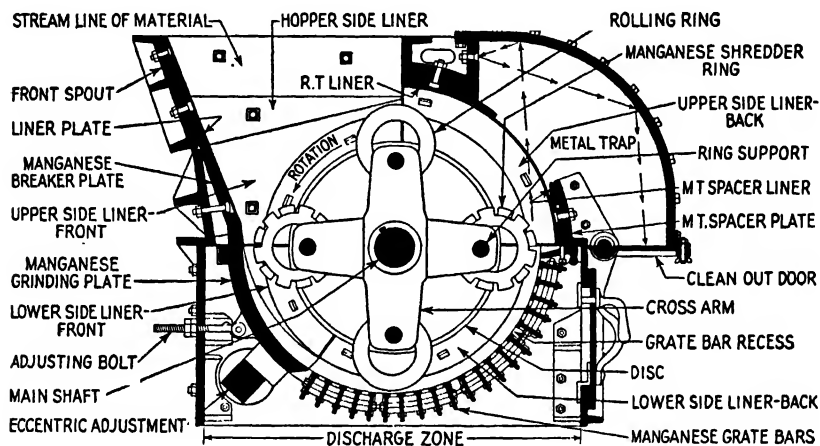


FIG. 13.—Rolling Ring Mill. Courtesy American Pulverizer Company, St. Louis, Mo.

is in rapid movement, the rings tend to pull away from the rotor so that they come very close to the lining of the mill. They serve first as hammers and then as grinders, the material being caught and rolled between the rings and the lining of the mill. Centrifugal force exerts a powerful pressure through the rings on the material, but at the same time very hard substances can pass through the mill and be caught in the pocket provided for the purpose. Shredders are under-running hammer mills in which the hammers are replaced by pivoted bars, whose sharp corners and edges serve as knives.

A very old type of intermediate crusher is the pan mill, also called Chile mill, chaser, and edge runner. It consists of a shallow pan, or a circular track set in a pan, and one or more heavy wheels traveling in a circle of very short radius. The axles of these wheels are attached to a vertical shaft to which power is applied. Since the wheels or rollers are continually changing direction, a sidewise slip or shear is added to the crushing effect.

Pulverizing. Most fine grinding is accomplished by rubbing the material between two surfaces, either or both of which are in motion. Practically the only exception to this principle is the use of very high-speed hammer mills operating on coarsely granular material, in which the particles are broken up to a fine powder by impact.

The oldest type of mill used for fine grinding is the "buhirstone" mill, in which a diagonally grooved stone disk rotates above a similarly grooved stationary disk. The grinding members are usually of a hard

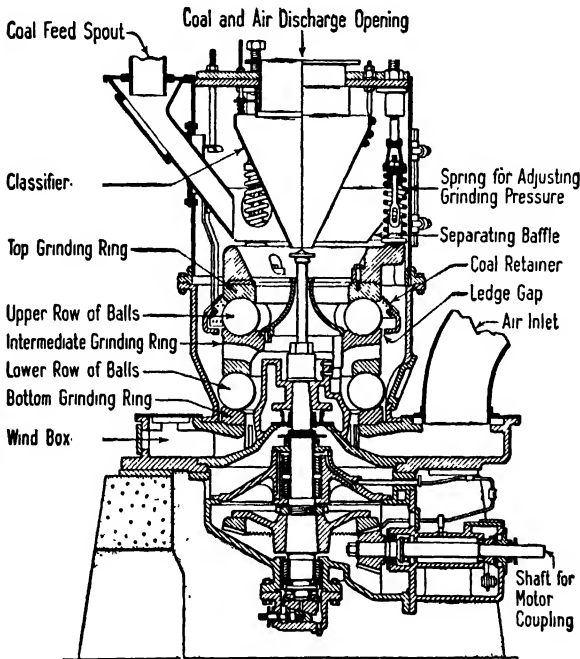


FIG. 14.-Babcock and Wilcox Pulverizer (Type B). Courtesy The Babcock and Wilcox Company, New York City.

variety of rock, but may be made of pressed abrasive material. Such mills are used extensively in the paint industry to grind pigments in oil.

The Bethlehem mill employs a series of rollers on the ends of stationary shafts under which a table rotates. The Babcock and Wilcox pulverizer, used largely in the coal industry, has two sets of balls within curved grinding rings. The upper and lower rings are in a fixed position, and the central ring is rotated. In the Raymond mill several rollers are at the ends of shafts, which are suspended and pivoted on the ends of horizontal arms extending from a central shaft.

As this shaft rotates, the pivoted shafts tend to stand out in a horizontal direction by virtue of centrifugal force. They are prevented from doing so by a ring, so that the rollers revolve against this ring and exert a powerful pressure on it. The material to be ground is picked up from the pan at the bottom of the mill by ploughs, which

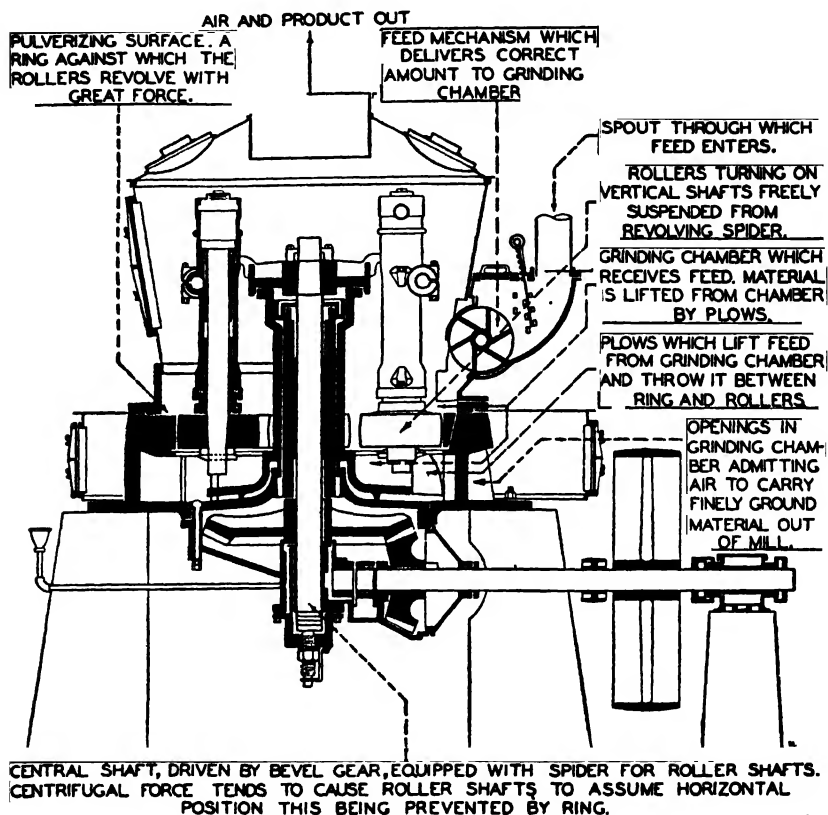


FIG. 15.—Raymond Mill. Courtesy Raymond Bros. Impact Pulverizer Company, Chicago, Ill.

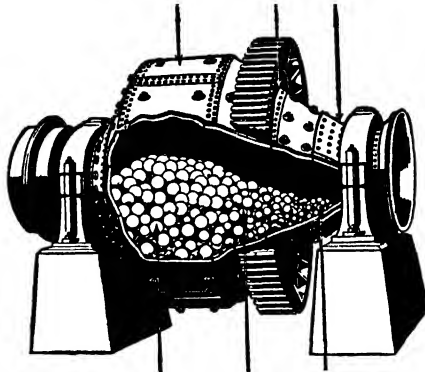
are attached to the central shaft, and which throw the solids up between the ring and the rollers. In all three types of mills just described the ground material is carried out by a stream of air for grading and classifying.

The simplest type of ball mill is a short horizontal cylinder in which coarse solids are placed, together with steel balls or quartz

pebbles, the cylinder being slowly rotated until grinding is complete. If the motion is too rapid, the balls cling to the inner surface of the cylinder and do no grinding. Part of the effect is in the rubbing of the solids between the rolling balls, and part is the impact of cascading balls. A tube mill is merely a ball mill whose length is several times its diameter. A rod mill uses instead of balls a number of parallel rods which are only a little shorter than the mill. When operated intermittently such mills are charged with coarse material and are run

DUE TO VARIATION IN PERIPHERAL SPEEDS IN CONICAL MILL, LARGE BALLS GRAVITATE TO LARGEST DIAMETER AND ONLY SMALL BALLS WILL BE FOUND IN CONE.

FEED DELIVERED TO MILL BY DRUM ROTATING WITH MILL, INSIDE OF WHICH IS A SCOOP WHICH DEFLECTS FEED INTO HOLLOW TRUNNION ENTERING MILL.



FINE PRODUCT DISCHARGED FROM MILL AT THIS POINT.

LARGE BALLS CRUSH COARSE FEED IN LARGE DIAMETER OF MILL WHERE GREATEST FORCE IS EXERTED DUE TO HEAVY BALLS DROPPING FROM MAXIMUM HEIGHT.

SMALL BALLS ARE FOUND NEAR DISCHARGE END WHERE FINER PARTICLES ARE DELIVERED, DUE TO SEGREGATION CAUSED BY ACTION OF THE CONE. ENERGY IS THUS PROPORTIONAL TO WORK REQUIRED.

FIG. 16.—Hardinge Mill. Courtesy Hardinge Company, Inc., New York City.

until the entire charge is ground to a fine powder, after which the balls are screened from the product.

Since there is a distinct advantage in continuous operation, it is possible to feed coarse material into one end of a ball or tube mill and to take out finely ground product at the opposite end. This necessitates some sort of screening system either within the mill or in the way of an outside screen operating in closed circuit within the mill, so that oversize may be returned for regrinding. Perforated linings surrounded by screens are used. The Hardinge mill has a very short cylindrical section with both ends conical. The shorter cone is at the feed end, and the longer at the discharge end. The balls must necessarily wear to some extent in all grinding operations, and as they grow small, and

finally disappear, new and unworn balls must be added. Thus all sizes of balls up to the maximum are always present. By virtue of the special shape of the Hardinge mill, distribution is attained so that the large balls are in the center and the smaller arranged in decreasing size along the longer cone towards the discharge end. The advantage of continuous over intermittent grinding is that the fine material is steadily removed, thus eliminating the cushioning effect of a powder in which larger particles are imbedded.

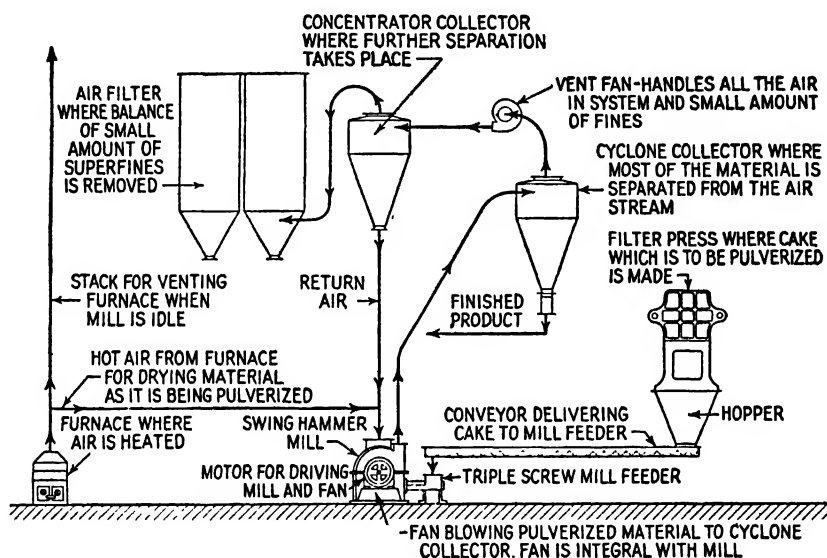


FIG. 17.—Combination of Drying and Pulverizing. Courtesy Raymond Bros. Impact Pulverizer Company, Chicago, Ill.

Some types of pulverizing equipment can be used for only relatively dry material; others operate either with dry material or very wet material in the form of a thin slurry. There is an intermediate stage in which a liquid causes the particles to stick together and form lumps. The problem of grinding damp solids in a high-speed hammer mill has been solved by passing a blast of heated air over the solids, drying them, and sweeping them through the mill. Pan mills, buhrstone mills, and all sorts of ball mills may be used advantageously with the material suspended in a liquid.

Dispersion. What is commonly referred to as dispersion combines disintegration with mixing. A very efficient method of mixing solids is to grind them together. Pigments are incorporated into paints by

grinding them with oil in buhrstone mills. The most widely used equipment for very thorough dispersion is the colloid mill. Some grinding is done by colloid mills, but they are commonly fed with finely ground solids that are to be incorporated and dispersed in liquids. Such solids are inclined to flocculate, and the function of the colloid

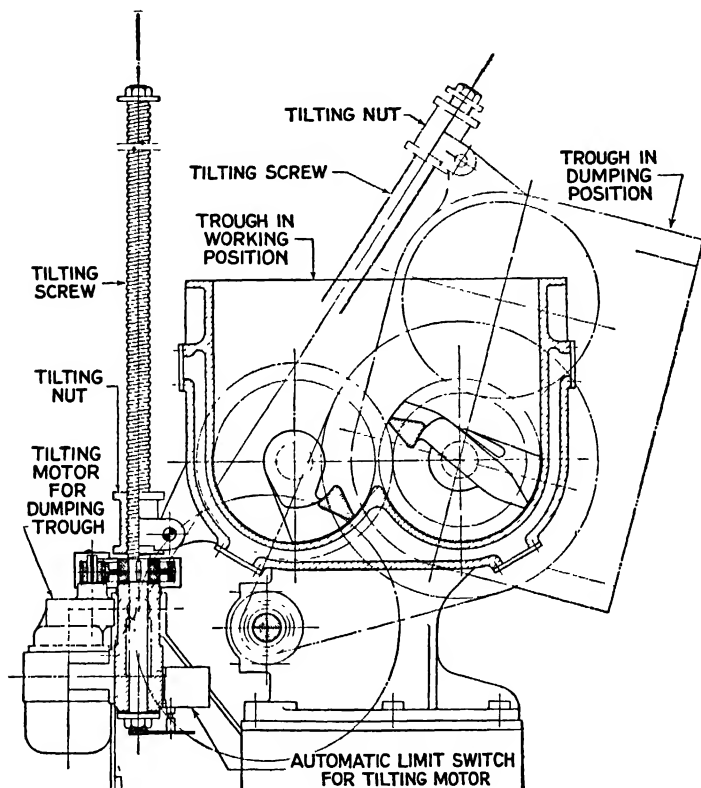


Fig. 18.—Werner and Pfleiderer Mixer. (Cross section.) Courtesy Baker Perkins Company, Inc., New York City.

mill is to bring about deflocculation. The shearing is largely done by the fluid. Immiscible liquids may be made into very stable emulsions by colloid mills. The principle of practically all colloid mills is that of a rapidly moving surface that is very close to a stationary surface, or of two rapidly moving and quite closely adjacent surfaces. Dispersion in such mills is very complete, and effects are obtained that are not possible in any other type of grinding and mixing equipment.

4. MIXING, KNEADING, AND AGITATING

Dry solids present difficult problems in mixing unless they are ground together. A common method of mixing solids is by the use of spiral conveyor flights in a closed trough, preferably two parallel conveyors moving in opposite directions. Materials are incorporated into a viscous or plastic mass by various types of kneading machines. The Werner and Pfleiderer mixer consists of a heavy, jacketed trough with

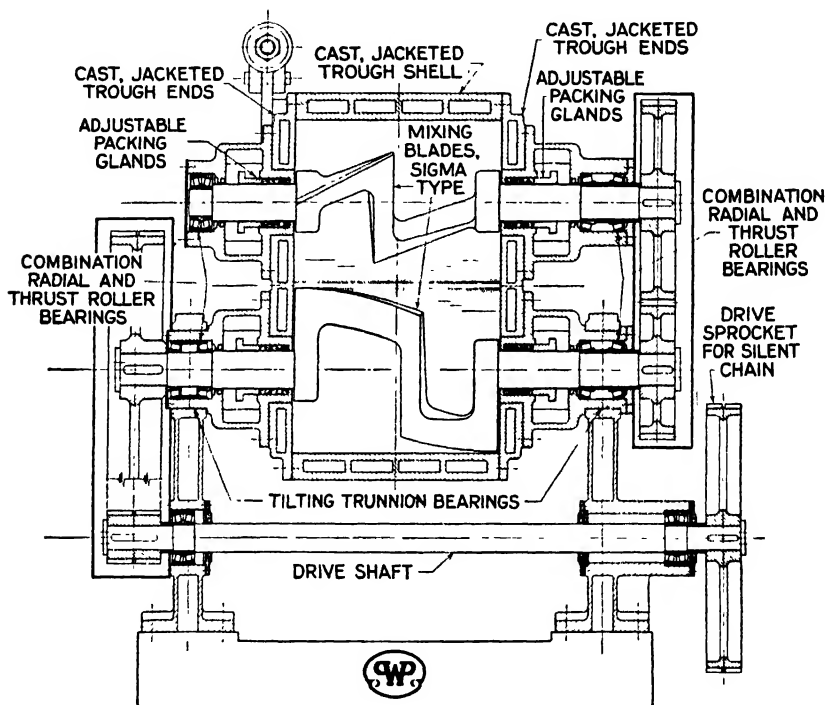


FIG. 19.—Werner and Pfleiderer Mixer. (Top view.) Courtesy Baker Perkins Company, Inc., New York City.

a ridge in its bottom dividing it into two shallow troughs of semi-cylindrical cross section. In each move mixing blades roughly of the shape of the Greek capital "Sigma" or a capital Z. The trough is arranged for tilting in order to discharge its contents.

For many years, rubber mixtures have been made on a pair of rolls revolving towards each other after the fashion of crushing rolls, but at different speeds. The rubber mixture clings to one roll in the form of a thin layer, while the excess piles up between the rolls. At

intervals the operator runs a knife across the rubber that coats the front roll and throws the segment that has been cut off to the opposite end of the roll. Solids and liquids are poured on the excess material between the rolls, and these are gradually worked into the mixture. A pan retains any material that falls through. The rolls are hollow and are equipped for temperature control by water circulation.

The Banbury mixer is now very commonly used in the rubber industry for the same purpose as mixing rolls, and is beginning to find

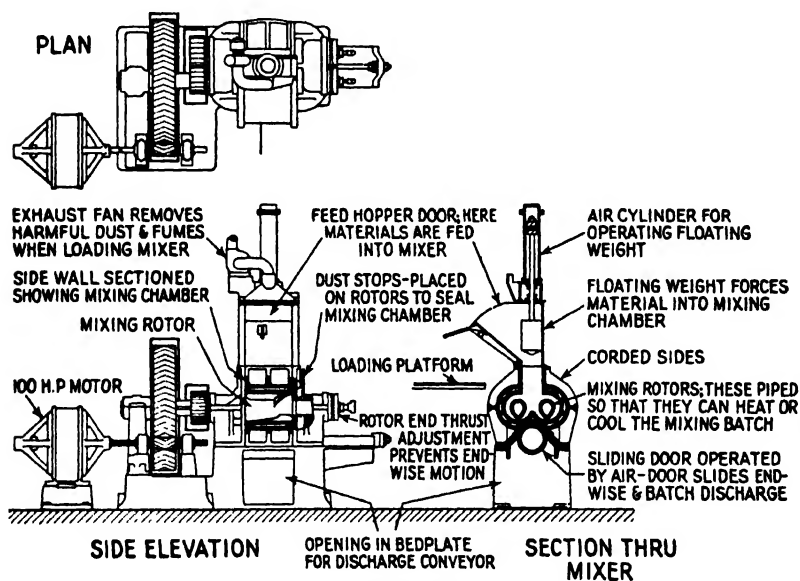


FIG. 20.—Banbury Mixer. Courtesy Farrel-Birmingham Company, Ansonia, Conn.

some application in the plastics, paint, and lacquer industries. The mixing chamber is double cylindrical in cross section and is equipped for temperature regulation. It has a ridge in the bottom forcing inter-composition of stock. The hollow mixing rotors are equipped for temperature control. The general cross section of the rotors is roughly pear shaped so as to provide acute converging surfaces with the mixing chamber. A floating weight retains material in the mixing chamber. At the end of the operation a door in the bottom of the mixing chamber slides endwise to permit discharge of the finished batch. This machine provides uniformity of mixing effect not possible by any other means, when used on stocks which become plastic while being worked.

Agitation is commonly carried out by paddles or propeller blades

on a shaft, but may be accomplished by circulating pumps or by blowing gases through the liquid. The Turbo Mixer employs impeller blades rotating within a ring equipped with deflecting blades, agitation being exceptionally thorough and complete. The Dorr Agitator is essentially a Dorr thickener in which the settled solids are withdrawn from the bottom and allowed to drop through the liquid until soluble material has been removed.

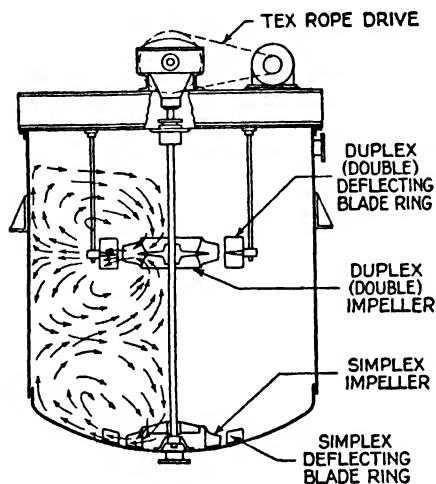


FIG. 21.—Turbo Mixer. (Cross section.)
Courtesy The Turbo Mixer Corporation,
New York City.

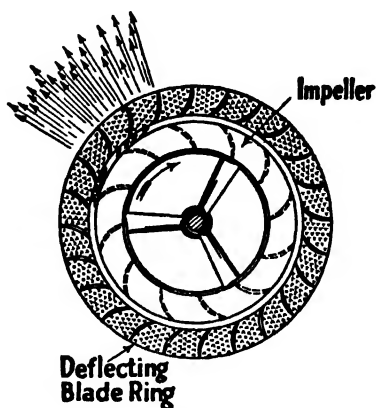


FIG. 22.—Turbo Mixer Impeller and
Ring. Courtesy The Turbo Mixer
Corporation, New York City.

5. MECHANICAL SEPARATION

This division includes a number of different types of separation, all of which depend on the physical properties of the materials, and in which there is no phase change.

Membranous Separation. The use of a membrane of some sort to bring about separation of solids from each other or solids from liquids includes screening, filtration, and dialysis.

Screening. Solid particles may be separated on the basis of their relative sizes. Screening depends on the use of woven or perforated membranes whose openings are of such a size that they are larger than the diameter of the particles to pass through them and smaller than the diameter of those to be retained, the assumption being made that the particles are of approximately uniform diameter in all directions. Larger screens are designated by the actual width of opening in inches

or fraction of an inch down to one-fourth of an inch. Smaller screens are designated by the number of openings per linear inch. In the latter case there must be a fixed relationship between the size of opening and the size of the wire of which the screen is made. This relationship has been established by the United States Bureau of Standards for 200-mesh screens so that the wire has a diameter of 2.1×10^{-3} in. and each opening a width of 2.9×10^{-3} in., thus giving 200 openings per linear inch. With this as a basis, most modern screen makers maintain the relationship of doubling each opening area with each succeeding larger size of screen so that each linear opening width is 1.414 (or $\sqrt{2}$) times that of the one just below it. If closer separation is desired below 65 mesh, the ratio of the fourth root of 2 may be used.

A screen analysis is accomplished by a set of screens with the coarsest at the top and the finest at the bottom over a collecting pan. Shaking and tapping are done by cams, eccentrics, and hammers. The amount remaining on each screen is weighed and also that in the collecting pan, and the report is in terms of the amount on and through each mesh size.

Inclined parallel bars over which a mixture of lumps and fines is passed constitute a "grizzly." Screens that operate with dry material of varied particle size differ from each other primarily in the method of agitating the material and vibrating the screening surface. Circular screens set horizontally and made up of several sections of different mesh size or different openings are known as "trommel" screens. They have the disadvantages that they afford the maximum size of opening to a particle pulled directly downward by the force of gravity only through a very limited segment of the entire circle of revolution, and that the feed is at the end having the finest mesh and the least ability to endure the battering of large particles. The majority of screens used in the chemical industry have flat screening surfaces and are operated in an inclined position. The frame may be fixed and rigid, and a part or all of the screen surface vibrated mechanically. Means of vibration include the use of hammers, eccentrics, and electromagnets. In the Tyler Hummer screen a section of the screen surface is attached to an electromagnetic vibrator and only this taut section vibrates, the remainder being stationary. The entire screen may be given vertical and oscillating motions by eccentrics. In addition to these motions the Rotex Screener vibrates the surface by means of soft and resilient rubber balls segregated in compartments below the screen and resting on a coarse supporting screen.

The removal of fine dust from gases by means of several layers of cloth in the form of tubes or bags is also referred to as filtration. The opening between the threads of fabric is much greater than the size of the dust particles, but impact of the particles against the fibers causes loss of inertia, and they drop out of the gases.

Filtration. Solids are commonly separated from liquids by filtration, which is based on the principle of interposing in the path of the

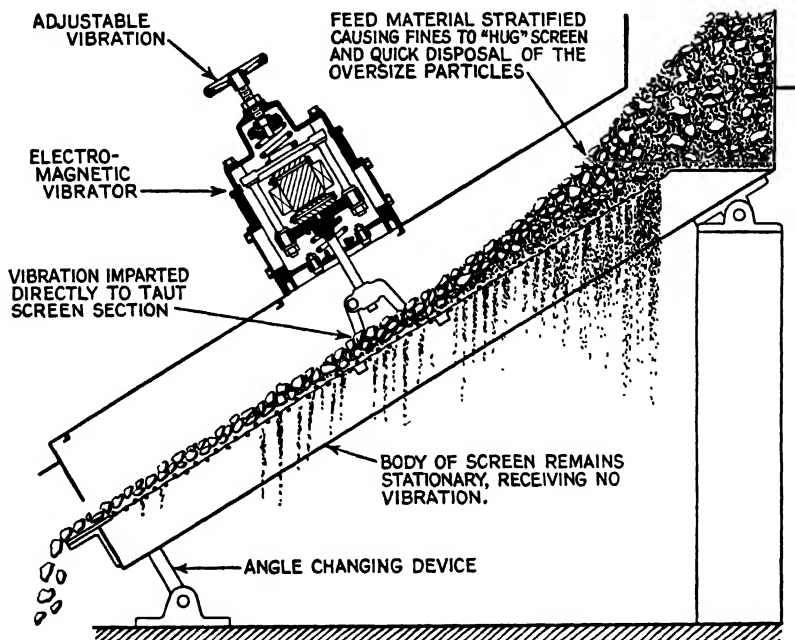


FIG. 23.—Tyler Hummer Screen. Courtesy W. S. Tyler and Company, Cleveland, Ohio.

suspension a membrane which will prevent the passage of the solids while permitting the liquid to go through. The membranes may be loose and granular, felted, woven, or porous. It is probably rarely the case that the openings in the filtering medium are smaller than the particles filtered, but the solids become entangled after the fashion of a log jam and build up their own filtering medium.

Sand and gravel filters may operate on the force of gravity alone, this being the case in many large installations for the filtering of public water supplies; or pressure may be employed with closed containers. The uppermost layers are made up of fine sand supported by increasingly coarser material. Liquids are drawn off from perforated pipes

equipped with strainers. Removal of undesirable solids from water is often aided by the use of iron and aluminum salts whose hydrous oxides are formed at the proper hydrogen ion concentration. Sand and gravel filters are cleaned by reversing the flow of water, removing the upper layer of sand, and washing it free of impurities. Porous ceramic material functions in much the same way as sand, but finds somewhat limited use in the chemical industry.

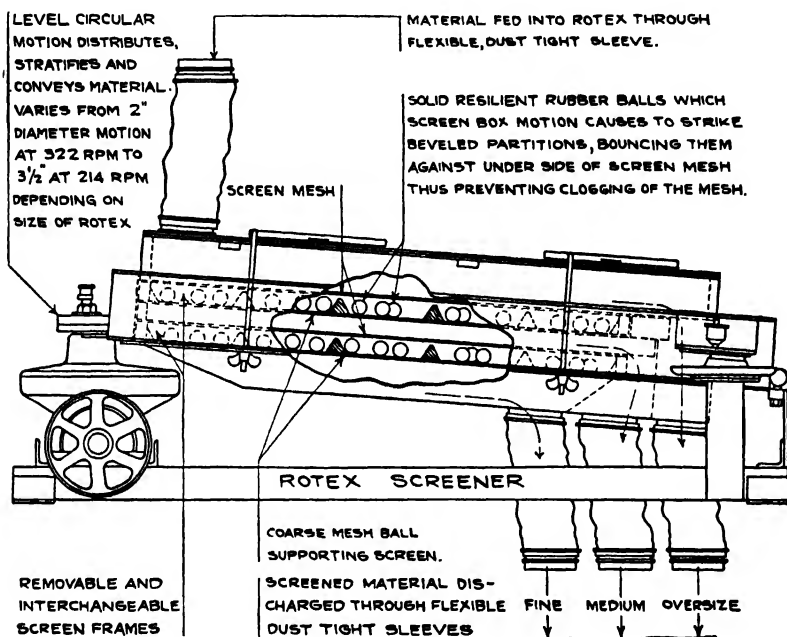


FIG. 24.—Rotex Screener. Courtesy The Orville Simpson Company, Cincinnati, Ohio.

The bulk of industrial filtration is accomplished by means of woven fabric, either of cloth or metal, supported on a rigid surface. The suspension is forced through the membrane either by atmospheric pressure in open filters or by positive pressures greater than atmospheric in closed filters. Division of filters into vacuum and pressure types is a convenient classification.

The simplest type of leaf filter is generally known as the Moore dipping leaf filter. Each leaf is made up of a cloth bag stretched over a frame of perforated pipe and reinforced by separating strips. A number of leaves in a single frame and connected by hose with a vacuum pump are dipped into a tank containing the suspension.

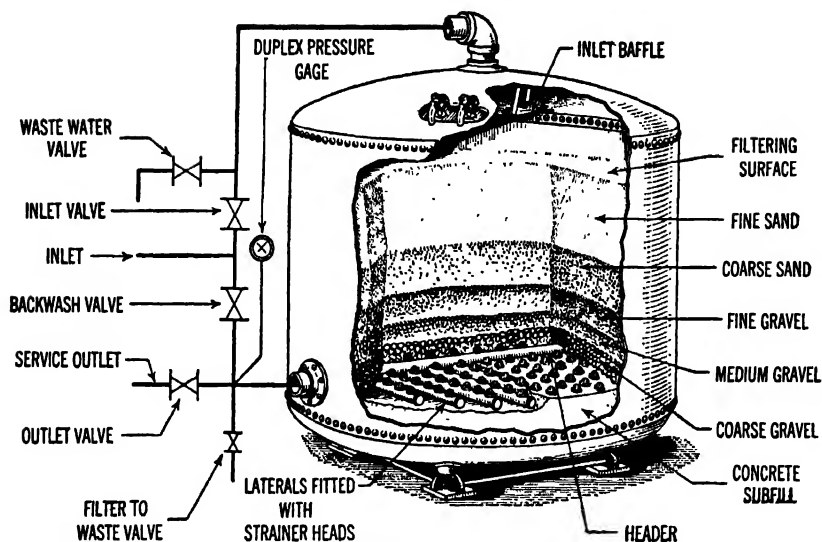


FIG. 25.—Sand and Gravel Filter. Courtesy The Permutit Company, New York City.

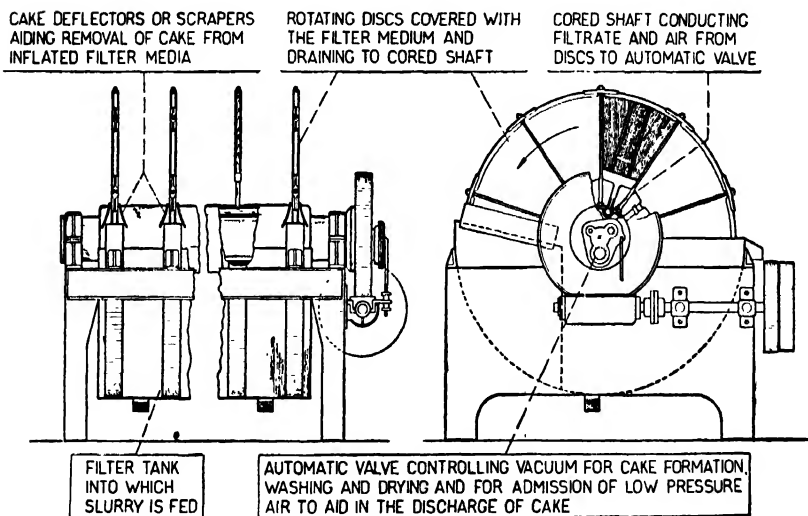


FIG. 26.—American Vacuum Filter. Courtesy Oliver United Filters, Inc., New York City.

Atmospheric pressure drives the liquid through the cloth, and the solids accumulate in a cake on the outside. When a sufficient thickness has been attained, the unit is lifted out and placed in a second tank of water for washing. The leaves are finally swung out over a discharge hopper; air is drawn through to bring about partial drying; and the current is then reversed to cause the cake to drop off.

The same general principle is applied to all continuous vacuum leaf filters. In the American vacuum filter several fan-shaped leaves make up continuous disks, but each leaf is separately connected to the proper channels in a hollow shaft, and functions individually. The

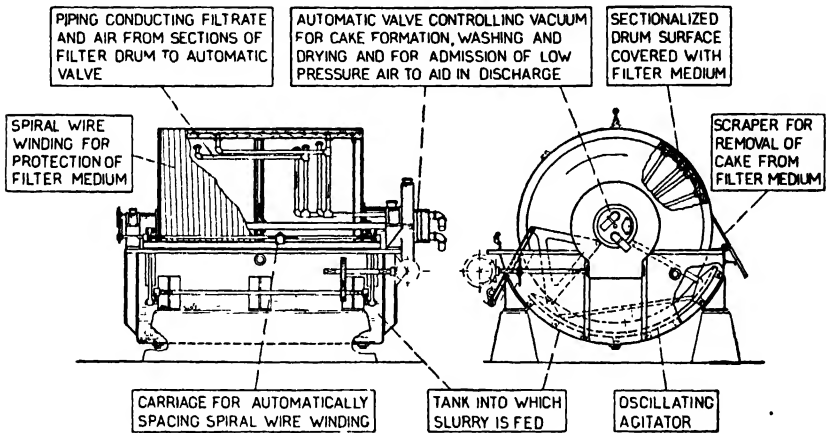


FIG. 27.—Oliver Vacuum Filter. Courtesy Oliver United Filters, Inc., New York City.

disks turn in a tank of special shape containing the suspension. Suction is applied to those that are below the surface, and this is continued as the leaves rise from the tank. Water is sprayed on the cake, the channel now being connected to a separate opening in a disk valve at the end of the cored shaft. Air is drawn through the cake, and as the leaves approach the surface of the suspension, a reverse current loosens the adhering solids and they are scraped off and discharged.

Very much the same principle underlies the drum type of filter of which the Oliver vacuum filter is a well-known example. Instead of separate leaves the entire surface of a horizontal drum except each end is perforated and covered with cloth reinforced by spirally wound

wire, or is made of heavy and fairly closely woven wire screen. Beneath this perforated surface are several separate parallel compartments, each connected to a cored shaft. A circular tank equipped for agitation holds the suspension, and in this the filter drum is partially immersed. Each compartment with its fabric-covered outer surface functions as a separate leaf. The same cycle of filtering, washing, drying, reverse of air current to loosen the cake, and discharge by scrapers characterizes this type of filter.

In the Dorreo vacuum drum filter the suspension is inside the rotating drum, which functions both as tank and filter. The solids are

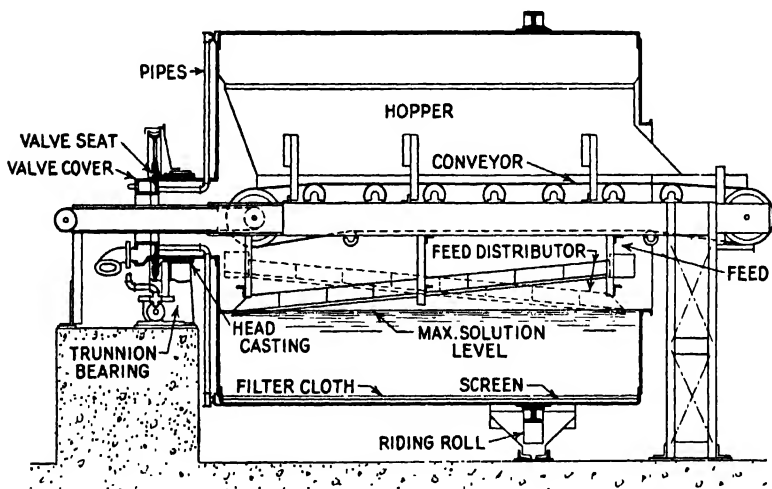


FIG. 28.—Dorreo Vacuum Filter. Courtesy The Dorr Company, Inc., New York City.

scraped off into a hopper in the upper part of the drum and removed by a screw conveyor. In this filter the segregation of particles by size is taken advantage of to give good filtering conditions, the coarse particles being next to the filtering surface.

Coarse crystals may be dropped into a series of open compartments on a drum, the bottoms of which are perforated and connected to a cored shaft. As soon as the liquid is drawn off, hot air is blown over the crystals, and by the time the crystals are dry, the drum has turned sufficiently to allow them to discharge by gravity. Such a filter may be visualized as radial Buechner funnels.

All pressure leaf filters are intermittent in operation. The leaves

are enclosed in a shell, and pressure is applied by a pump to the suspension. The various types differ mainly in the forms of leaves and shell, in the method of opening and closing, and in the way in which the cake is removed.

In the Kelly pressure filter, vertical rectangular leaves are held parallel in a horizontal cylindrical shell with one removable head, the leaves being attached to the head and supported by a frame running on rollers inside the shell. After cakes of sufficient thickness have accumulated on the leaves and washing is complete, the shell is drained, pressure is relieved, and the movable head and leaves are pulled back so that the cake may be scraped off into receiving troughs.

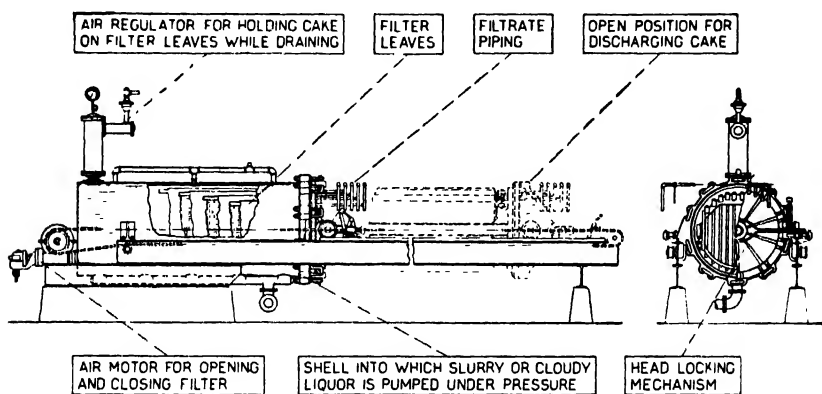


FIG. 29.—Kelly Pressure Filter. Courtesy Oliver United Filters, Inc., New York City.

The Sweetland pressure filter has circular leaves suspended within a horizontal shell made in two sections, the upper one being fixed and the lower one counterbalanced and arranged to drop down to permit discharge. The suspension enters the bottom of the filter, and the filtrate from each leaf passes out at the top through a sight glass and into a common discharge manifold. When the cakes are formed and washed, the shell is drained, and the lower half is loosened and dropped. Nozzles on a rotating pipe serve to flush the solids from the surface of the leaves. An eccentric shaft tightens all bolts uniformly. Each leaf has an individual cutoff valve in case of a break in the fabric.

Rotating leaves attached to a cored shaft and within a shell characterize the Vallez and the Sweetland Cantilever pressure filters. In the Vallez filter the upper half of the shell lifts in order to give access

to the leaves, but discharge is accomplished without opening the shell, the cake being flushed off into a trough equipped with a screw conveyor. The Sweetland Cantilever filter has a removable head with all leaves attached to it, so that they are drawn out when the head is pulled back, and the cake may be flushed off. Rotating the leaves gives uniform quality of cake where different size particles tend to segregate.

A filter press is essentially a series of shallow compartments whose vertical walls are lined with fabric. The suspension is pumped into these compartments under pressure, the solids are either retained on

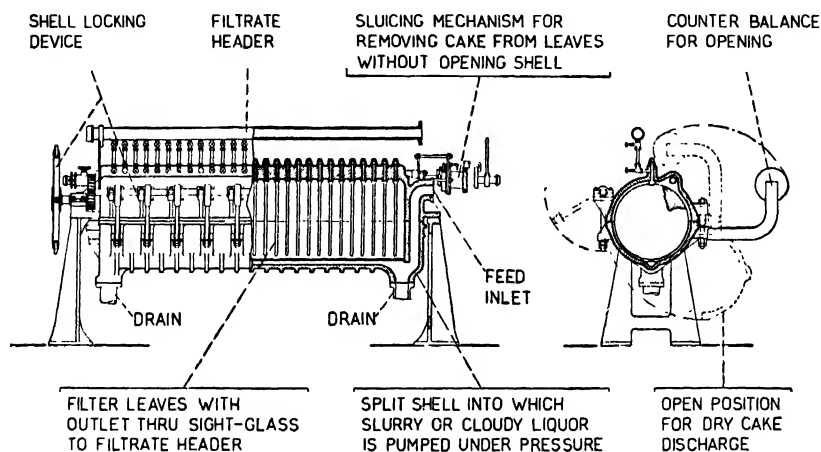


FIG. 30.—Sweetland Pressure Filter. Courtesy Oliver United Filters, Inc., New York City.

the walls as a thin layer or constitute a cake filling the whole compartment, and the filtrate runs down the solid walls behind the fabric and escapes through openings at the bottom of the press. These compartments are made up either by covering a number of recessed plates with cloth and pressing them together, or more commonly by employing cloth-covered flat plates and interposing between them frames of the same size, pressing the whole firmly between a fixed and a movable head. The cloths serve as packing material to prevent leakage. The plates and frames are supported and aligned by projections resting on side rails.

The suspension of solids is forced in through the fixed head, thence passes through a continuous channel made up of coinciding holes

through each plate and frame, and usually enters each compartment through openings in the frames connected with the main channel. When recessed plates are used, either with or without frames, the feed is admitted by connecting each compartment with the next by a hole in the recessed portion of each plate. The cloth is firmly attached around each opening by flanged nuts called "grommets." The filtrate passes over the surface of the plates and escapes through a diagonal channel connected either with an individual drainage cock or with a common discharge channel.

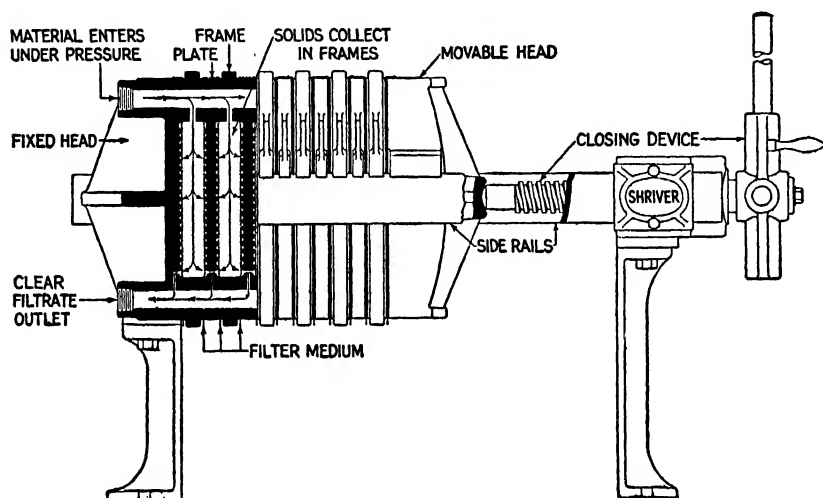


FIG. 31.—Plate and Frame Filter Press. Courtesy T. Shriver and Company, Harrison, N. J.

Washing in a filter press may be of the same type as in all other filters previously described, that is, by causing the wash water to follow the same path as the filtrate. This is known as "simple washing." In a filter press another type of washing, commonly called "thorough" washing, is made possible by equipping alternate plates with special inlet channels, which admit the wash water back of the cloth. By closing the drainage cock on each plate that has a wash inlet channel, the liquid is forced through the cloth, the cake, and the cloth on the next plate before it can escape through an open cock. Some presses are equipped with separate wash outlets on alternate plates.

Dialysis. Semipermeable membranes are capable of separating certain substances from others, those passing through ordinarily being

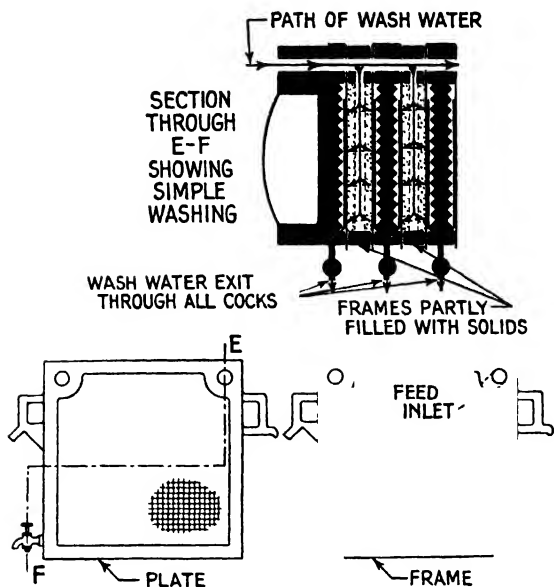


FIG. 32.—Simple Washing in Filter Press. Courtesy D. R. Sperry and Company, Batavia, Ill.

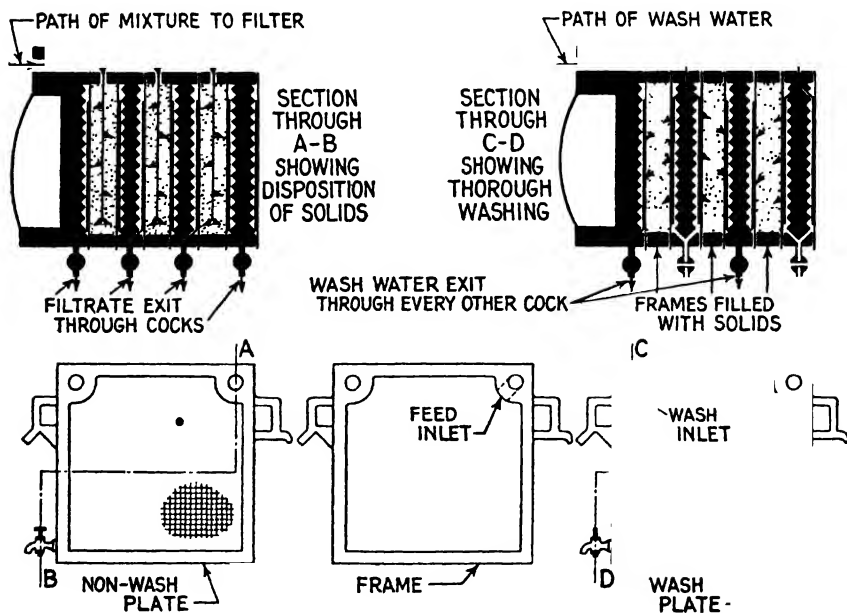


FIG. 33.—Thorough Washing in Filter Press. Courtesy D. R. Sperry and Company, Batavia, Ill.

crystallizable solids and those remaining behind being colloidal in their nature. At one time, dialysis was employed to recover sugar from beet molasses, but is now confined largely to the recovery of caustic soda in rayon manufacture and to the production of serums. The equipment resembles a filter press, the water and the liquid from which material is to be removed being in alternate compartments separated by membranes such as parchment.

Settling. Settling may be natural, retarded, or accelerated, and includes such operations as the use of air for separation; accelerated

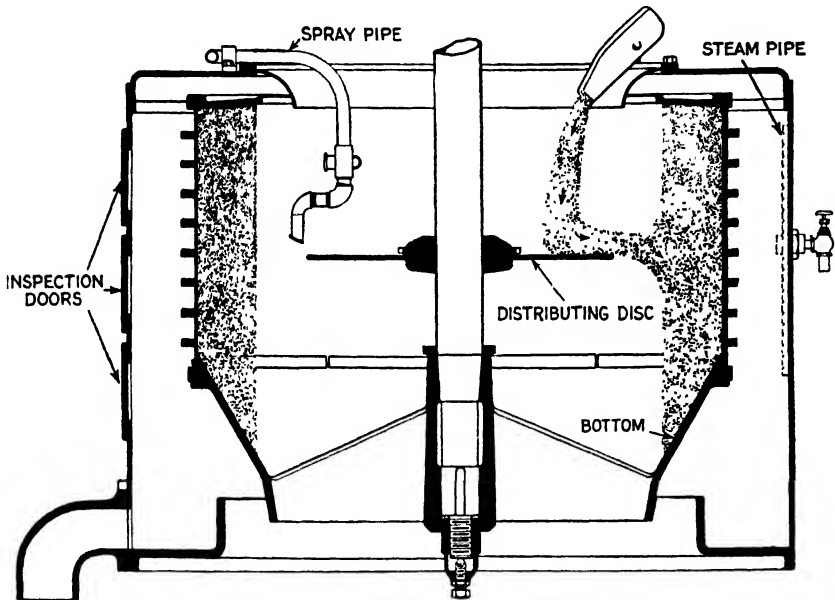


FIG. 34.—Fletcher Centrifugal with Lewis Open Bottom Basket. Loading Operation. Courtesy Fletcher Works, Philadelphia, Pa.

settling by centrifugal force either of solids from liquids or liquids from liquids that are immiscible; natural settling in thickeners; alteration of apparent specific gravity in flotation operations; and classification by differential settling rates.

Air Separation. Solids may be separated from air in settling chambers, but it is more common practice to impart a rapid whirling motion to the dust-laden air in "cyclone" separators. The larger dust particles are thrown against the walls of the separator and are removed, while the air carrying finer material passes on to settling chambers and bag filters. By altering the pressure of the gas, its dust-carrying capacity

is changed, and separation of particles according to size is accomplished.

Centrifugal Separation. Solids may be removed from liquids and immiscible liquids may be separated by employing centrifugal force, these two being examples of accelerated settling. Since the force is proportional to the radius of revolution and to the square of the peripheral velocity, it is possible to use forces much greater than those employed even in filtration. The usual type of centrifugal for the

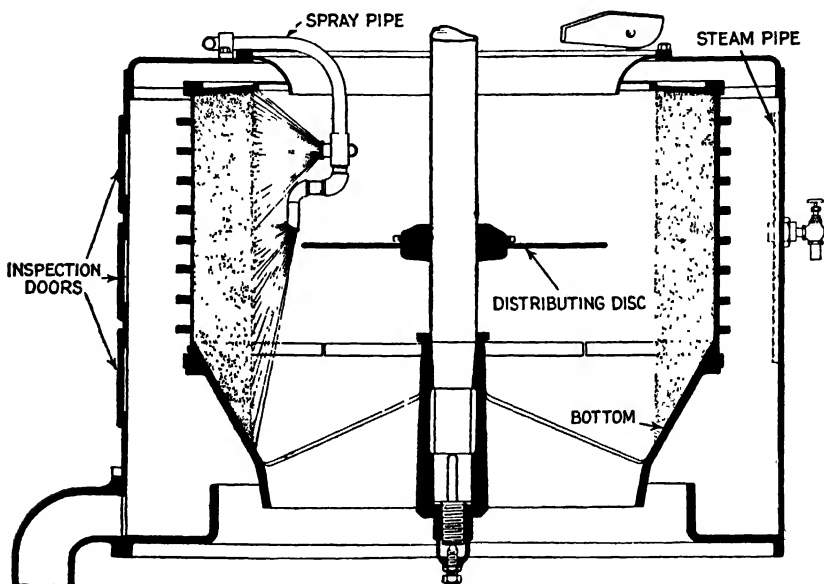


FIG. 35.—Washing Operation. (See Fig. 34.) Courtesy Fletcher Works, Philadelphia, Pa.

separation of solids from liquids (also called a hydroextractor) is a short, vertical cylinder or "basket" with perforated side walls revolving within an outer shell. The bottom of the basket may be closed except for a discharge valve, or it may be entirely open. The basket is attached to a central shaft, which is driven either from above or below. The solids are charged into the centrifugal while it is in motion to insure even distribution, and the speed is increased after the charging is complete. Inequalities in loading are compensated by self-balancing devices. The speed of a centrifugal of this type is of the order of 750 revolutions per minute. The solids are held on the perforated surface, while the liquids are forced through the openings

into the annular space around the basket. Centrifugals are ordinarily intermittent in their operation, but several types are continuous. In the Elmore centrifugal, scraping blades continuously move the solids down the walls of the basket to the discharge opening. The Laughlin centrifugal has a horizontal basket fed with a screw conveyor, and discharge is by means of spiral scraping blades.

Immiscible liquids of nearly the same specific gravity and tending to form emulsions may be separated by the use of centrifugal force.

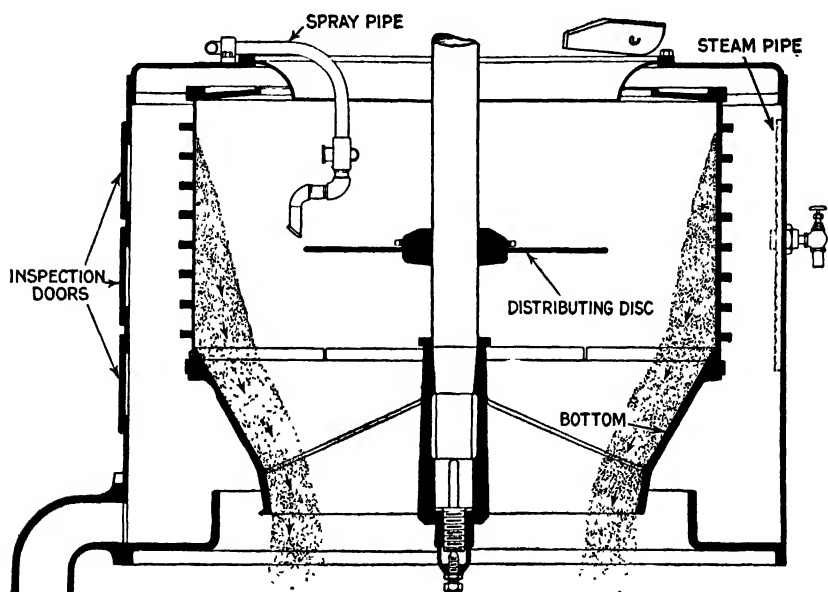


FIG. 36.—Discharging Operation. (See Fig. 34.) Courtesy Fletcher Works, Philadelphia, Pa.

The equipment used in such separations is commonly called a centrifuge. Small amounts of solids are also removed from liquids in the same type of machine. In the Sharples Supercentrifuge a vertical cylinder, called a bowl, and rotating at a very high speed (15,000 r.p.m.) is fed at the bottom with the mixture of liquids, which may or may not contain some solids. The heaviest material, the solids, is thrown to the wall and remains there. The heavier liquid forms an annular layer along the wall of the bowl, and moves to the top where it discharges through an opening at the outer edge of the bowl into a collecting and discharge chamber. The lighter liquid flows upward

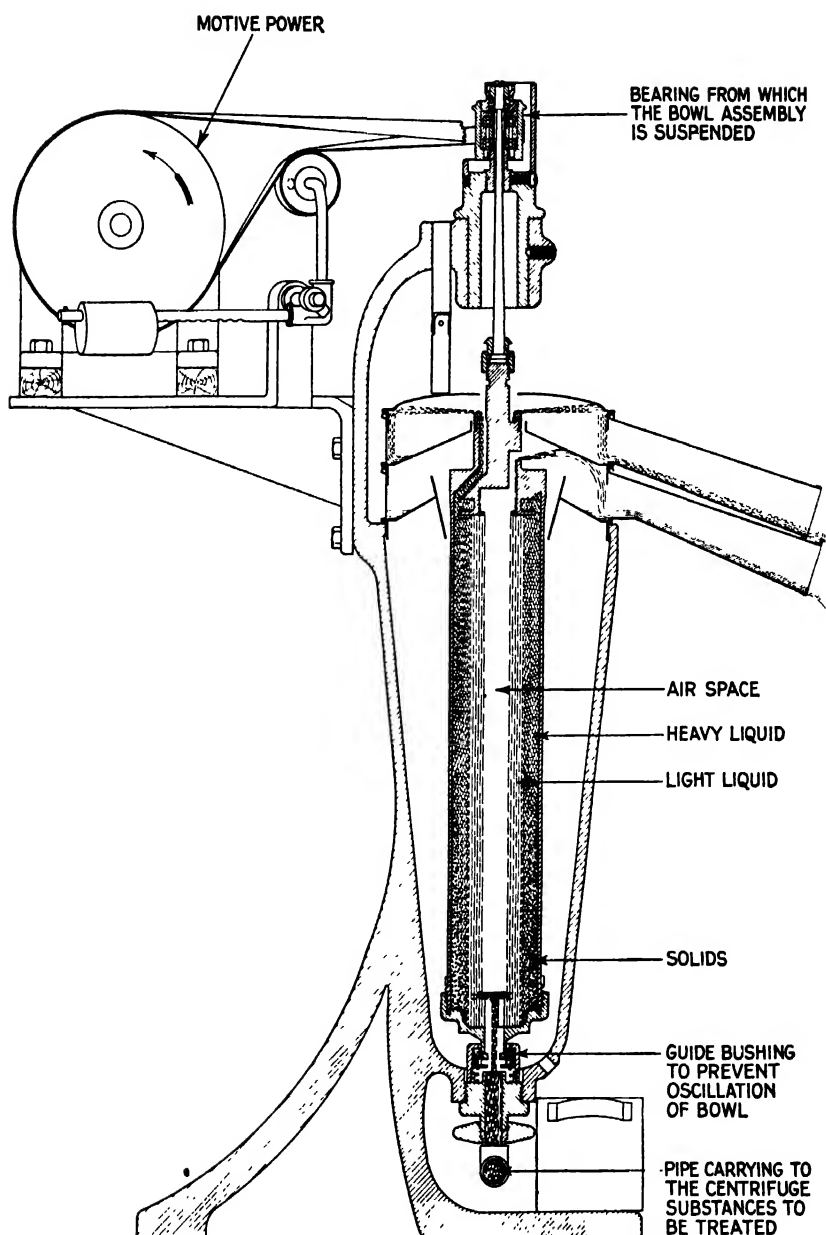


FIG. 37.—Sharples Supercentrifuge. Courtesy The Sharples Specialty Company, Philadelphia, Pa.

as an inner layer and discharges through an opening near the center of the bowl. There is an air space in the center of the bowl.

Thickening. Slow continuous settling of solids from liquids and removal of a mud is spoken of as thickening. This process is commonly employed with suspensions relatively low in solids. The Dorr thickener is made up of a tank or basin or a set of superimposed shallow basins equipped with slowly moving scrapers radiating from a central shaft. The suspension is fed in near the center of the tank; a clear liquid overflows at the top into a circular trough called a "launder"; and a thick mud is raked to the center and discharged by a diaphragm pump. Such thickeners may be used in sizes up to 350 ft. in diameter, and in such cases the rakes are driven by a small tractor

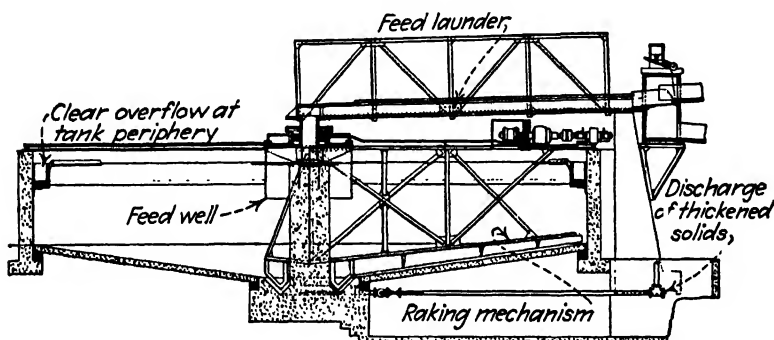
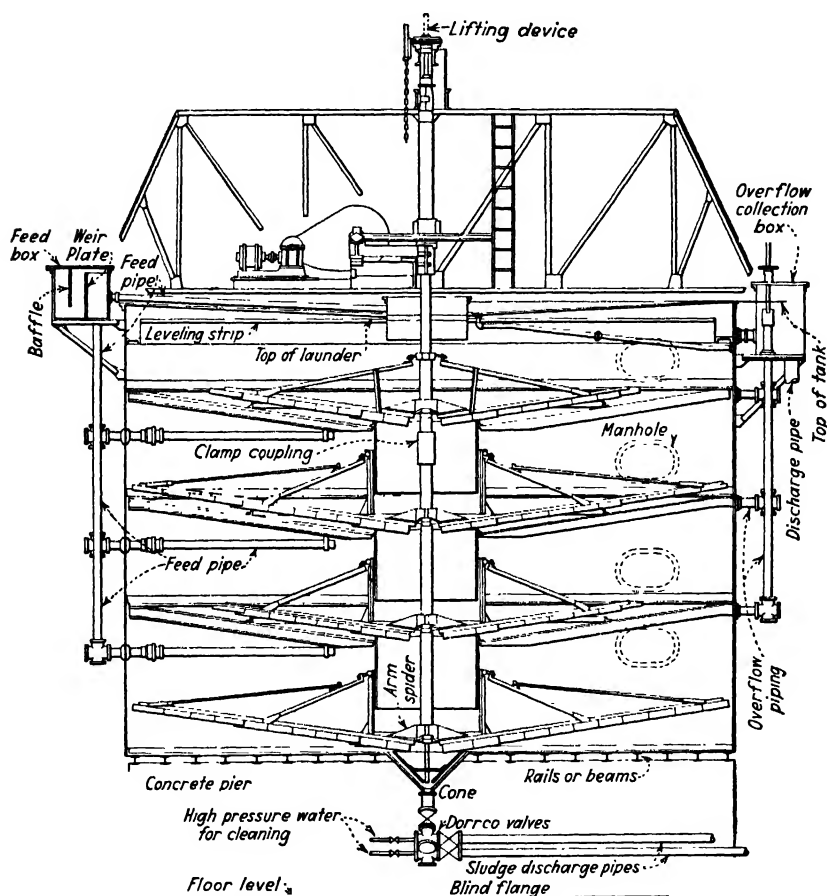


FIG. 38.—Dorr Traction Thickener. Courtesy The Dorr Company, Inc., New York City.

moving around the circumference of the tank. By employing rake arms with hinged ends equipped with springs, rectangular tanks may be used. The Hardinge thickener has a bed of sand on the thickener bottom. A clear liquid is drawn from below the sand filter bed, and a spiral blade, lowering slightly at each revolution, removes the accumulated solids and some sand to a discharge well at the center. Other thickeners function much after the fashion of leaf filters, employing tubular filtering members and intermittently dropping the accumulated solids to the bottom of the tank.

Flotation. Solids may be separated from liquids, and in some cases classified according to their chemical composition, by processes grouped under the general term "flotation." Badger and McCabe classify these processes as: surface-tension methods depending on selective wetting by water, those particles that are wetted settling and those that are not wetted floating; bulk-oil methods based on prefer-

ential wetting of some particles by oil to enable them to rise to the surface; and froth-flotation, in which a permanent froth is produced by bubbling air through a mixture of mineral powder, water, and oil. In this last and most widely used method the mineral is adsorbed on



Sectional Elevation

FIG. 39.—Dorr Tray Thickener. Courtesy The Dorr Company, Inc., New York City.

the surface of the bubbles, which have a highly viscous interface. The froth is broken up by thickeners or vacuum drum filters.

Classification and Table Concentration. Particles may be separated from each other by free or hindered settling in liquids. By flowing a suspension through a succession of boxes of pyramidal shape and

increasing size (Spitzkasten), the decreasing velocity of the liquid brings about settling of the coarsest particles first and the finest last.

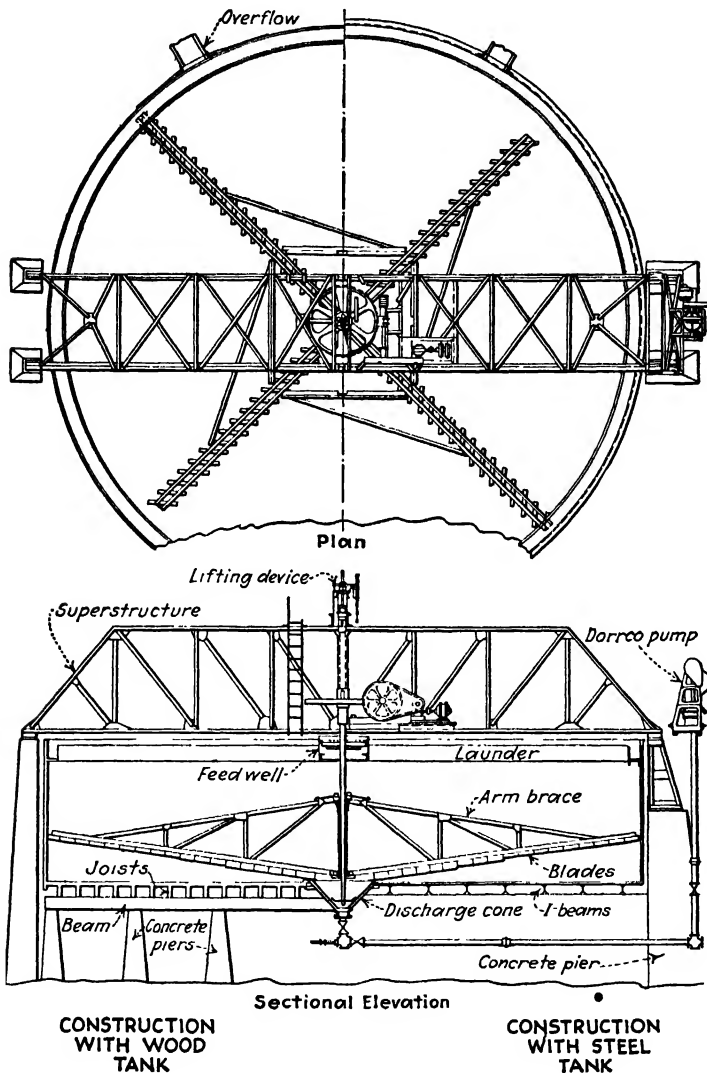


FIG. 40.—Plan and Elevation of Dorr Thickener (showing types of construction).
Courtesy The Dorr Company, Inc., New York City.

The Dorr classifier serves to separate a relatively small amount of coarse material from a larger quantity of fine particles. It is essentially a long, inclined, shallow box equipped with a number of con-

nected rakes. The suspension is fed in near the middle of the box, and the particles settle at a rate governed by their size. Coarser particles tend to carry down fines mechanically. The rakes stir the mass of settled material and drag it up the inclined surface. Each individual rake moves only a short distance, rises, and comes back to its original position. The coarser material is thus pulled along the bottom, while the particles are washed free and overflow in suspension from the lower end of the classifier. The coarse particles are pulled out of the liquid, drained, and finally discharged at the upper open end. Several

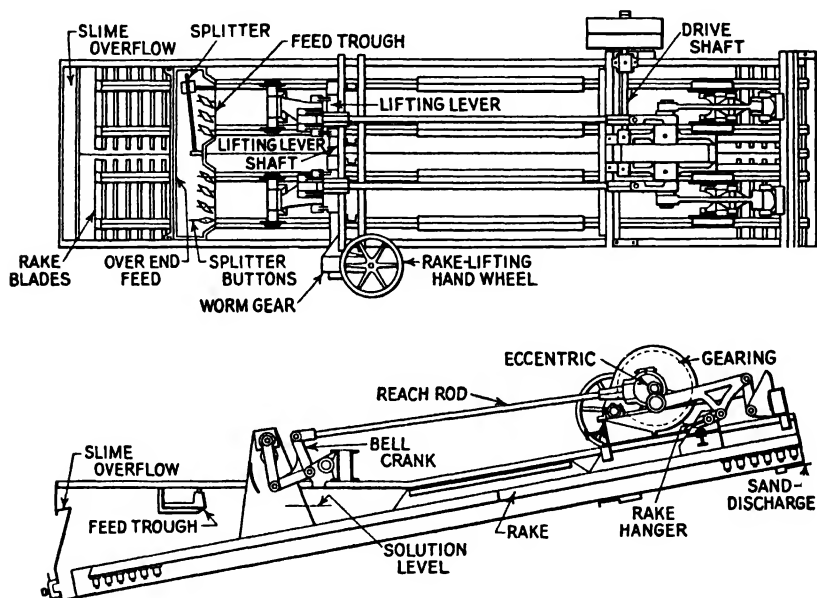


FIG. 41.—Dorr Classifier. Courtesy The Dorr Company, Inc., New York City.

classifiers may be used in series (multiple-deck). The Dorr classifier finds extensive use in closed-circuit wet grinding, and also in removing grit from clay and pigments.

A hydraulic jig combines a screening surface with hindered settling, water being moved up and down quite rapidly through the material on the screen. Separation is partly by size and partly by difference in specific gravity. The Wilfley table is essentially a flat and slightly inclined surface equipped with a number of parallel cleats of gradually increasing length. The suspension is allowed to flow over the table, which has a continuous jerking motion. The heavier particles settle into the space between the cleats and move as in a series of troughs

to the discharge end, while the fine particles are carried on in the liquid.

Selective Adsorption. The general operations of absorption and adsorption are discussed later in the chapter. It is possible to remove certain materials from a gas or a liquid by selective adsorption. This is probably best illustrated in the selective adsorption of organic coloring matter from sugar solutions by bone black and other active chars. The equipment is essentially a closed vertical shell filled with char on mats and grids through which the colored solution passes.

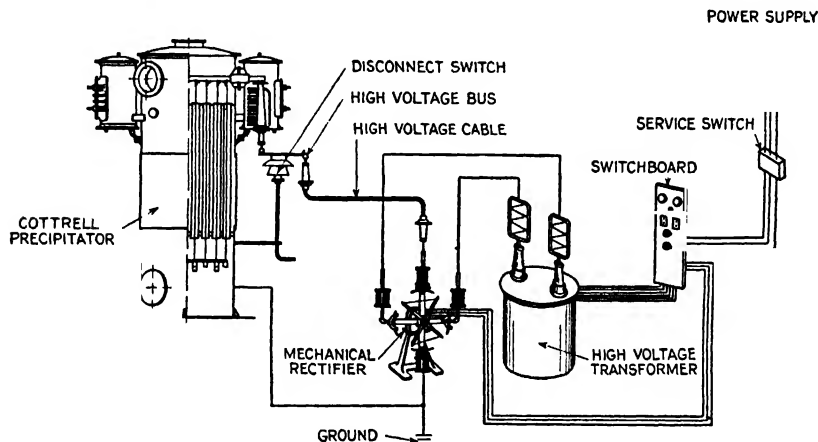


FIG. 42.—Cottrell Electrical Precipitation Process. Diagram of Electrical Equipment. Courtesy Research Corporation, New York City.

Electrical Separation. *Electromagnetic.* Substances that are susceptible to the action of an electromagnet may be separated by being brought into a magnetic field. A very common application of this principle is in the removal of tramp iron from the feed of a crusher. The conveyor belt passes over a magnetized pulley and discharges all material that is not affected by a magnet, while iron clings to the belt and is carried a short distance further before it passes out of the field and drops off. Magnets beneath which a belt runs at right angles to a belt conveyor lift magnetically susceptible material from the conveyor. When the material is out of the magnetic field the belt drops it to one side. Magnets at the bottom of depressions in a trough may remove similar material from a flowing suspension of solids.

Electro-osmotic. The relative rate of diffusion of ions through semipermeable membranes under the influence of an electrical poten-

tial has limited use in chemical industry. Water may be largely freed of dissolved material by this method.

Electrostatic. Many mists and suspensions of solids cannot be removed from air by absorption in water or by filtration, since each particle is covered by an adsorbed film of air. Such particles, however, readily take up gaseous ions produced by a silent, high-voltage electrical discharge. The particles thus charged are swept to a discharge electrode, where they coalesce as they lose their electrical charges. The current used is around 65,000 volts, is unidirectional, and is pro-

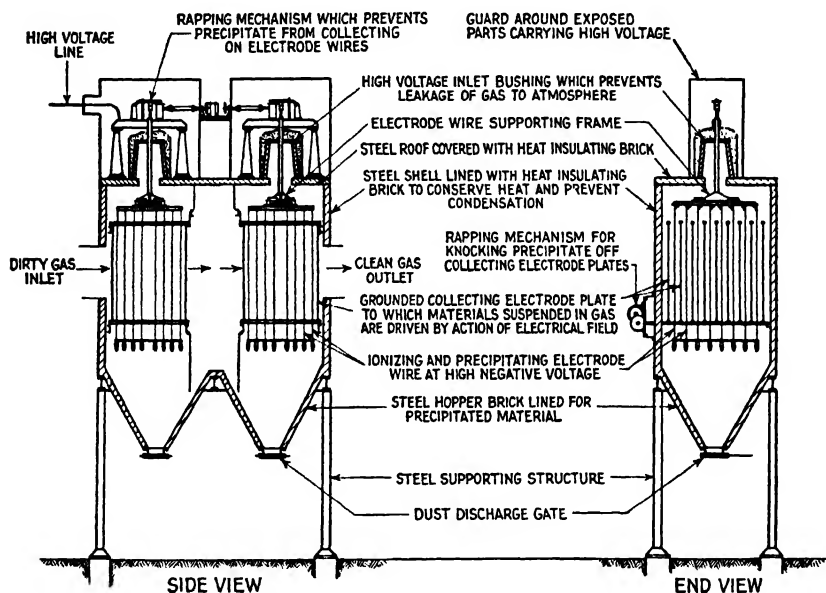


FIG. 43.—Hot Roaster Type Precipitator. (See Fig. 42.) Courtesy Research Corporation, New York City.

duced by a synchronous converter in which current is taken from an alternating source at the maximum points of the sine curves. Hence current flows only a part of the time. The discharge electrodes are either tubes or plates, while rods or wires of irregular surface function as charging electrodes. The collected material, if a liquid, flows from the surface of the collecting electrode, or if a solid, is shaken off at intervals, the flow of current being interrupted. The use of electrostatic precipitation is referred to in other chapters in connection with rather varied processes.

6. PHASE CHANGE SEPARATION

Drying, crystallizing, evaporating, and distilling all involve the principles of equilibrium between phases. In all cases, changes of phase permit mechanical separation. Drying involves the removal of liquids by vaporization from a relatively large amount of solids. Crystallizing has to do with formation of saturated solutions and

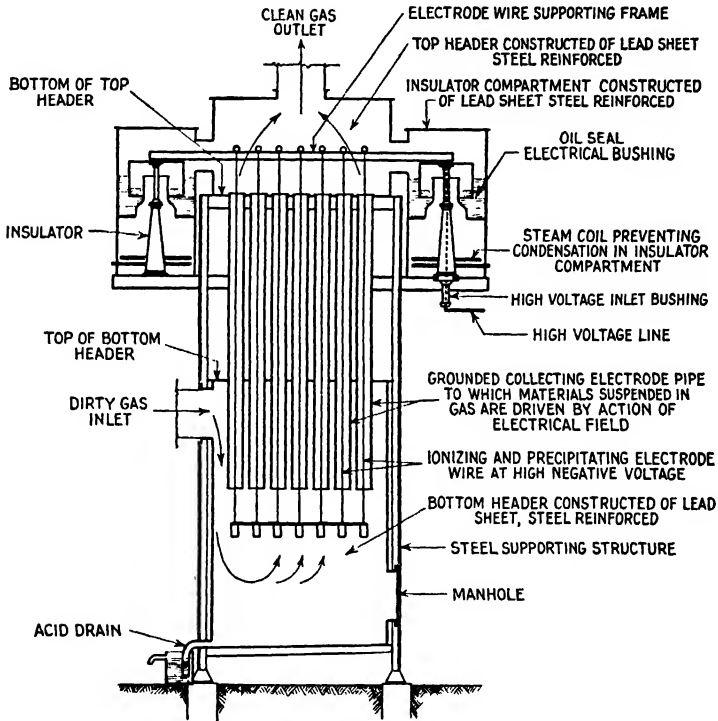


FIG. 44.—Acid Mist Precipitator. (See Fig. 42.) Courtesy Research Corporation, New York City.

removal of dissolved material by the conversion to the solid phase. Evaporating includes the concentration of solutions for the purpose of recovery of solvent, solute, or both. Distilling is for the purpose of separation of liquids by means of their differences in vapor pressure.

Drying. The removal of liquids from damp solids is spoken of as drying. The liquid commonly removed is water. The factors involved include diffusion, humidity of gases, surface evaporation, and vapor pressure lowering.

A "loft" dryer is merely a room in which material is placed and allowed to dry without any regulation. Cabinet dryers are equipped for the passage of air of definite and carefully regulated temperature and humidity. Loose crystalline solids are commonly spread in thin layers on trays or shelves, and air heated by steam coils is passed over the material. Vacuum dryers are extensively used in order to take advantage of more rapid diffusion of vapor into a vacuum; to recover valuable solvents; and to protect heat-sensitive materials. These dryers are essentially strongly built cabinets with closely fitting

doors, and are equipped with steam-heated coils under trays or with hollow steam-heated shelves, with condensers, and with vacuum pumps.

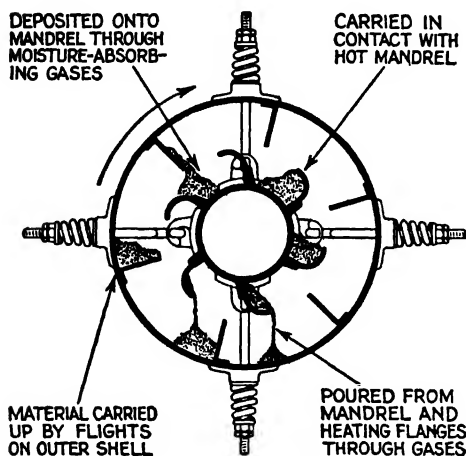


FIG. 45.—Tyler-Hamor Dryer. Courtesy W. S. Tyler and Company, Cleveland, Ohio.

Continuous dryers are characterized by uniform and uninterrupted flow of material through them. Tunnel dryers operate on the principle of drawing the material, supported on trays loaded on trucks, through a long compartment or tunnel, and passing a current of heated air in the opposite direction. Belt, bucket, or

platform conveyors may also be used. Solids may be removed from a vacuum drum filter by means of belts made up of woven wire or parallel strings. Damp solids may be scraped from such a filter and packed into a belt made of interlacing links. The solids conveyed by any of these methods pass through a continuous dryer, the belt hanging in festoons. When drying is complete, the solids are removed by kinking or tapping the belt.

Solids that are not heat-sensitive are dried in rotary atmospheric dryers, which are steel shells slightly inclined from the horizontal position. Hot gases pass through such dryers while they revolve slowly. If direct contact with furnace gases is to be avoided, the material may pass through an annular space around a central compartment carrying the gases. The material is stirred and distributed by shelves or flights attached to the shell, their function being to carry

the solids to the upper part of the shell and drop them through moving gases. It is also possible to surround a rotating shell by hot gases, the shell being housed in a brick setting.

Rotary dryers are also operated under reduced pressure, heat being applied both from an outside steam jacket and a hollow shaft carrying stirring and scraping blades. Vacuum drum dryers operate with a thin suspension of solids in a liquid, and may thus be thought of as evaporators. They consist of a heavy shell in which one or two hollow, polished drums rotate. The liquid is fed on to the surface of each drum at such a rate as to form a very thin layer. The drums are steam-heated, and by the time they have passed through an arc of

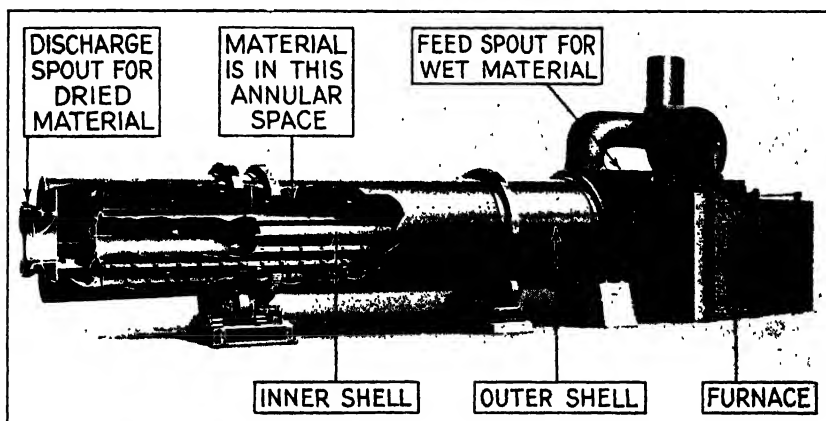


FIG. 46.—Ruggles-Coles Rotary Dryer. Courtesy Hardinge Company, Inc., New York City.

250° the liquid has completely evaporated. The solids are then scraped off and discharged to a receiver. By employing two receivers, one may be kept under vacuum while the other is shut off for discharge. Spray dryers also function as evaporators. The suspension is broken up into a fine spray, a common method being by feeding it on a rapidly whirling disk. In especially designed equipment it is possible to use the cooling effect of evaporation while removing liquid from heat-sensitive substances, such as rubber from latex and milk powder from skim milk, and at the same time to employ comparatively high temperatures. The spray falls through heated gases, which rise through the dryer.

Crystallizing. Soluble substances may be isolated in relatively pure form by dissolving them in a suitable solvent and altering the

temperature to bring about lowering of solubility. In many cases, dilute solutions undergo evaporation before crystallization takes place. Crystallizers are either of the batch or continuous type. If a saturated solution is run into an open tank and allowed to stand, crystals will separate, but are apt to occlude impurities and to be of inconvenient size. Stirring during crystallization and provision for cooling are essential features of modern batch crystallizers. The Swenson-Walker continuous crystallizer is an open, semicylindrical trough equipped with water jacket and spiral agitators. The cooling water in the jacket flows counter-current to the hot concentrated solution. The agitator lifts the crystals as they form and allows them to fall through the solution. Crystals are removed from the end opposite where the feed enters, either by flowing out with mother liquor or by being lifted

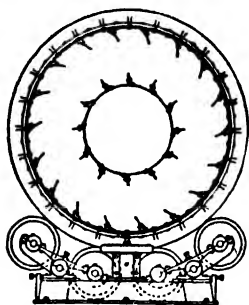


Fig. 47.—Cross Section Ruggles-Coles XA Dryer. Courtesy Hardinge Company, Inc., New York City.

out by a screw conveyor. Crystallization may take place under reduced pressure in closed vessels, the evaporation or “flashing” of the liquid being an efficient means of cooling the solution. Crystallization often takes place in vacuum evaporators, and thus will be referred to again.

Evaporating. Evaporating may be carried out at atmospheric pressure, but reduced pressure is probably more commonly used in order to take advantage of low-pressure or exhaust steam. Superheated steam, hot gases, hot liquids of high boiling point, radiant heat, and electrical heat are also employed to evaporate

liquids. Solar evaporation has some use in dry climates in connection with the production of sodium chloride from sea water. Evaporation may be facilitated by allowing liquids to flow over large surfaces exposed to hot gases. A very common device for evaporating liquids is to pass them down a tower packed with quartz or stoneware shapes, and to pass hot gases up through the tower. This is the common method, for example, of concentrating sulfuric acid.

In order to avoid excessive heating as well as to utilize low-pressure steam, a great deal of evaporation is carried out under reduced pressure. A vacuum pan or evaporator is a closed vessel heated by steam in, or surrounded by, tubes or coils, and is equipped with devices for breaking foam and separating mechanically entrained drops of liquids from vapors. The evaporator is connected with a condenser and vac-

uum pump. Some evaporators operate with a considerable depth of liquid; in others there is very little liquid at any one time, so that evaporation takes place from thin films. Even where there is a large amount of liquid, a part of the evaporation is from a mixture of vapor and liquid in tubes.

Steam is the most common source of heat in vacuum evaporators. It is either within tubes or coils that are surrounded by the liquid, or the liquid to be evaporated passes through tubes surrounded by steam. In the "calandria" type of evaporator, of which the Swenson vertical tube evaporator is typical, a number of parallel tubes are connected with horizontal sheets. The central tube or "downtake" is quite large, and the remaining tubes are small. Steam surrounds the tubes; the cooler liquid in the center of the evaporator goes down through the downtake; and a froth rises through the smaller tubes as evaporation takes place. The heating section is known as the "calandria." The vapors and entrained liquid rise through the vapor space, pass through a centrifugal separator, often called a "catchall," and the vapors escape either to a condenser or to the heating section of another evaporator. In the "basket" type of evaporator a cylinder set concentric with the vertical evaporator shell contains the tubes, and the annular space between the cylinder, or "basket," and the evaporator walls functions as a downtake.

In the Zaremba horizontal tube evaporator, steam is within parallel horizontal tubes while the liquid circulates around the tubes. Headers are connected with tubes at each end. Steam is fed into one header and condensate and fixed gases removed from the other.

Film evaporators have relatively little liquid in them at any one time. Very long vertical tubes through which films of evaporating liquid rise represent the extreme in "climbing film" evaporators (Kestner). In these the liquid passes through the tubes only once. An inclined set of tubes of shorter length with large vapor space and an outside downtake permitting continual circulation constitute another film evaporator in common use (Buflovak). In the "forced-circulation" evaporator (Swenson) the bundle of tubes projects into the vapor space; the material which escapes from the tubes at high velocity strikes a curved deflector which causes the liquid to descend and separate from the vapors; and a pump brings about rapid circulation. This evaporator is said to be particularly suited for evaporating liquids that are viscous and inclined to foam and also for liquids that produce scale.

In another evaporator (Yaryan), liquid passes through horizontal

tubes surrounded by steam, and the froth escapes into a header equipped with baffle plates.

When evaporators are used with solutions from which crystals are continually separating, they are commonly equipped with "salt boxes," "salt legs," or separate settling tanks. A "salt box" is a reservoir

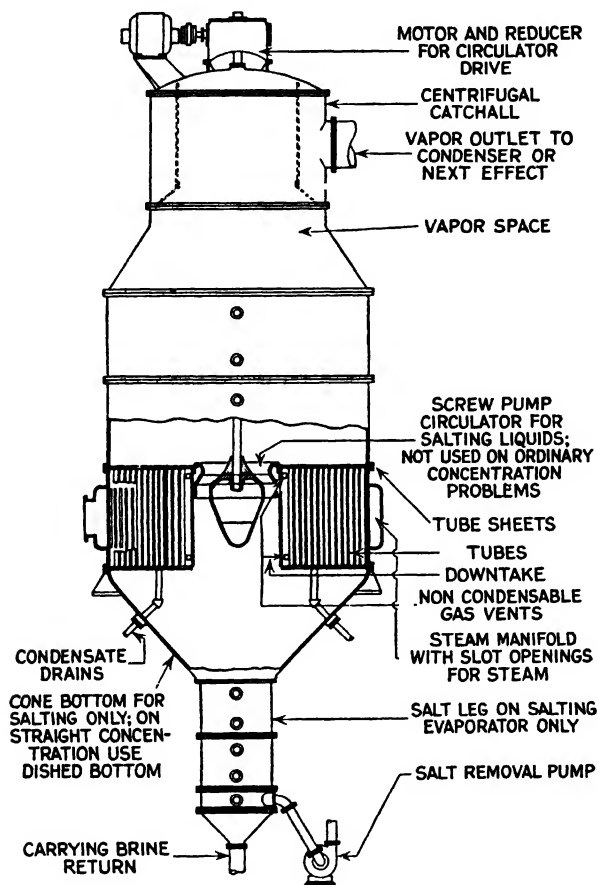


FIG. 48.—Swenson Calandria Type Vertical Tube Evaporator.
Courtesy Whiting Corporation, Harvey, Ill.

usually cylindrical and very much smaller than the evaporator, and is equipped with a perforated false bottom and a clean-out door. A "salt leg" is merely a long pipe leading down from the bottom of the evaporator and connecting with a bucket elevator. The salt leg must be of sufficient length to exceed the barometric height of the solution. Salting evaporators ordinarily have conical bottoms.

Neglecting slight heat losses from various sources as well as any considerations of superheat, a pound of steam should theoretically evaporate a pound of water. This water vapor again condensing gives out enough heat to evaporate another pound of water. If the vapors are run through a condenser, this heat is lost, and the original pound of steam does its work only once. If the vapor from one evaporator is passed into the tubes or coils of another evaporator operating under a somewhat lower pressure, it will condense, and the heat liberated will

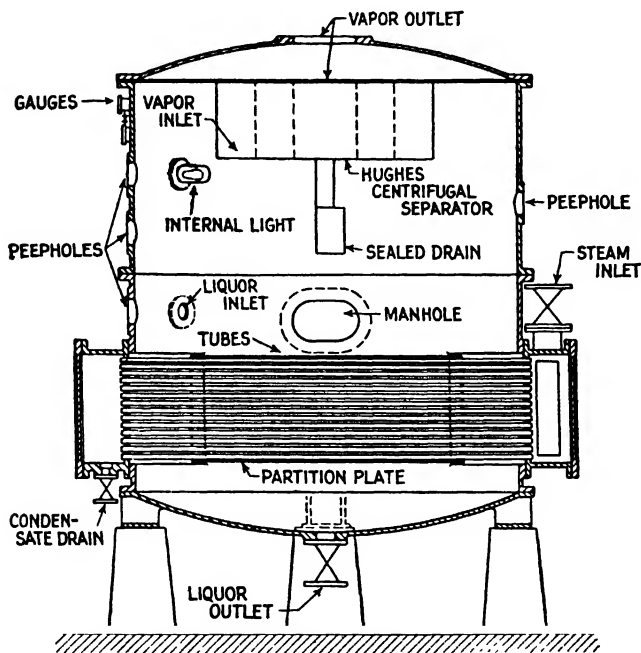


FIG. 49.—Zarembo Horizontal Tube Evaporator. Courtesy Zarembo Company, Buffalo, N. Y.

vaporize approximately the same amount of liquid in the second "effect." This principle is known in chemical industry as "multiple effect evaporation." One pound of steam used in the first of four evaporators thus connected will cause the vaporization of from 3.5 to 3.7 lb. of water. The factors determining the number of evaporators to be used in a given process include: superheat, due to the rise in boiling point caused by the concentration of solute and by hydrostatic head; cost of steam; and cost and upkeep of evaporators and accessories. Where steam is cheap, fewer effects are used, rarely more than four. Where steam is expensive, as on ocean liners, it is often the case

that as many as six evaporators are used in multiple effect for the production of distilled water. As the vapor from the first effect is condensed in the second to a liquid occupying a very small volume in comparison to vapor volume, a vacuum is produced without the use of a vacuum pump, and the steam space in the second effect serves as a condenser. Only one vacuum pump and one condenser are used, these being on the last effect. It is necessary to use a small pump to remove condensate from the steam space of each effect except the first, and the liquid being evaporated is commonly pumped from one effect to the

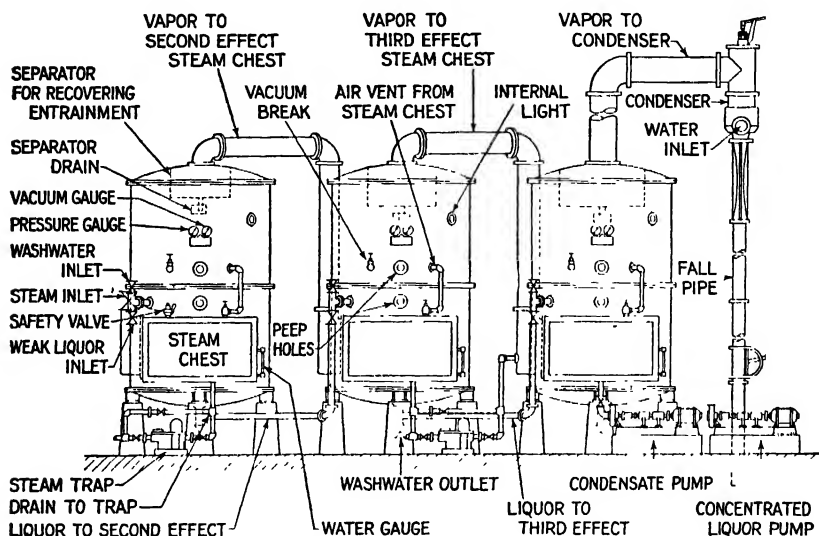


Fig. 50.—Multiple Effect Evaporation. Courtesy Zaremba Company, Buffalo, N. Y.

next. The nature of the solution being evaporated determines whether the flow of liquid shall be parallel with that of steam (forward feed) or in an opposite direction (backward feed). In the case of forward feed, pumps to move the liquor are necessary only on the first and last effects, but with backward feed, pumps are required for each effect. The viscosity of a liquid is less at higher temperatures, which is an advantage in backward feed operation. If the liquid is already hot when fed to the evaporating system, viscosity is not a determining factor. Forward feed with a cold liquid means excessive consumption of steam, since the temperature in the first effect is highest. With backward feed the liquid is heated by steam which has already evaporated some liquid, and the temperature interval through which it is raised is less.

Distilling. Separation of liquids by means of differences in vapor pressure constitutes what is known as distillation. Immiscible liquids give off vapors of constant composition regardless of the relative quantities of the two liquids present. When the sum of the partial pressures of the two liquids equals that maintained above them, boiling takes place. The amount of each liquid in the distillate is determined by its molecular weight and its vapor pressure. Steam distillation involves passing steam through a liquid immiscible with water, and the effect is the same as distilling the high-boiling liquid under reduced pressure. Superheated steam is commonly used so that the sensible as well as the latent heat of the steam may be utilized. Certain binary liquid mixtures have vapor-pressure curves with a minimum point lower than that of the vapor pressure of either component of the same temperature. At this point a liquid of constant composition distills, and complete separation is impossible by ordinary distillation. Addition of a third component forming stable compounds with one of the components permits further separation, this being illustrated by the use of sulfuric acid in concentrating nitric acid. Those binary mixtures with a maximum point on the vapor-pressure curve permit partial removal of one component in pure form, but complete separation is not possible. A third component may change the entire system, permitting complete removal of one of the two required components.

Practically complete separation is possible in the case of a binary mixture whose vapor pressure curve lies between the vapor pressures of the two components. The vapor arising from a boiling binary mixture of this type is always richer in the component of higher vapor pressure, and thus of lower boiling point. By collecting fractions through very narrow temperature intervals and repeatedly redistilling, it is possible to bring about ultimate separation, but this procedure would be very costly and slow.

A modern fractionating column is a vertical cylinder divided by horizontal plates into a number of compartments, each of which functions as a still. These compartments communicate with each other by vapor pipes and by other pipes carrying liquids back to the next plate. The liquid-return pipes extend up through the plate to a lesser distance than the vapor pipes, and thus determine the liquid level which can be reached on a plate, and reach down into the compartment below to a point well under the liquid on that plate, thus preventing vapors from escaping through such liquid pipes. The vapor pipes are covered by bells that either have serrated or perforated edges, or that are supported at several points so as to leave a narrow opening for vapors.

The liquid-return pipe of the bottom plate either dips below the liquid in the still or has the shape of a J to serve as a trap to prevent escape of vapor. The topmost compartment connects with the condensing system of the still.

Regardless of the general method of operating a column, whether intermittently or continuously, this is what takes place at any instant on a given plate. Vapor passes up through a series of pipes, is de-

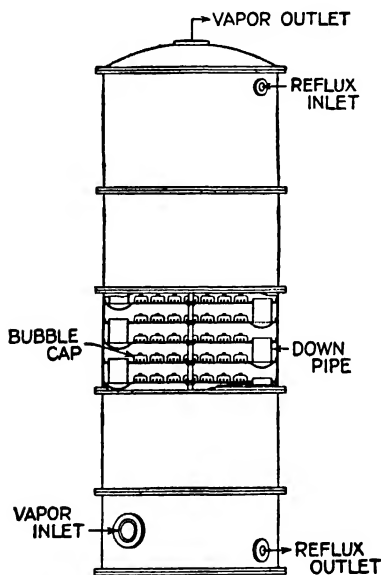


FIG. 51.—Bubble Cap Fractionating Column. Courtesy F. B. Badger and Sons, Boston, Mass.

flected by the bells over the pipes so that it bubbles through a layer of liquid on the plate. It condenses, and the heat given out causes an equivalent amount of vapor to be formed, which contains more of the volatile component than does the liquid from which it comes. The condensed liquid is supplemented by a supply from the plate immediately above it. As this liquid loses some of its more volatile component, it overflows and runs down the liquid pipes reaching below the level of the liquid on the plate below it. The net result of the action on each plate is that a liquid progressively richer in the less volatile component works its way down the column, and vapors progressively richer in the more volatile component work their way up the column, until the material

that reaches the condensing system is practically pure low-boiling liquid. The degree of purity attained depends largely on the specifications for the products.

There are two methods of carrying out fractional distillation by means of a bubbling column. One is batch or intermittent, in which the mixture to be distilled is heated in a still and a sufficient amount of the distillate returned from a partial condenser to maintain an adequate amount of liquid flowing down the column. Since the composition of liquid and vapor is continually changing, it is necessary to increase continually the ratio of the amount returned to the amount collected as final product. The second method, and the one more generally used, is continuous fractionation. Assume that a unit such as

the one previously described is run as an intermittent still until the liquid on the bottom plate is practically pure high-boiling material, and the vapors from the top plate are made up of the more volatile component. Between these two extremes are mixtures of different composition on each plate. By taking samples it may be ascertained which plate has a liquid corresponding exactly to the composition of the mixture to be distilled. By feeding the mixture continuously at this point it is possible to maintain a fixed ratio of reflux to product finally condensed, and thus to draw from the still the less volatile material and from the final cooler the more volatile material. By utilizing the feed as a cooling medium in heat exchangers through which both vapors and the very hot residues from the still pass, a great deal of heat is conserved. The heat losses, aside from the heat escaping through the insulation of stills and columns, are represented largely by the water drawn from the refluxing condensers and from the final cooler. Modern heat technology has resulted in enormous savings in those industries using distillation as a unit operation.

Where it is necessary merely to purify a substance containing non-volatile impurities rather than to separate two liquids by differences in vapor pressure, the operation is much simpler, and requires only a still, a condenser, and a receiver. The vapors of very high-boiling liquids may be condensed in air-cooled pipes. When liquids are apt to undergo undesirable chemical changes at elevated temperatures, it is common practice to carry out distillation under greatly reduced pressures, and also to avoid direct heating of the still. Heating may be accomplished by steam or hot liquids in jackets or in coils.

Stills include vertical cylindrical shells of somewhat the same type as vertical evaporator bodies; horizontal shells, such as those used in the petroleum industry; and pipe stills, composed of pipe in coils or straight tubes connected to common headers. Heat is applied by direct fire; by circulating hot liquids through coils, which are either in the walls of the still or more commonly in the liquid in the lower part of the shell; and by the use of steam admitted directly into the liquid through perforated coils.

Sublimation is somewhat akin to distillation, but refers to the vaporization of those substances that have high vapor pressures in the solid state, and which condense directly from a vapor to a solid. Condensation is difficult because of the insulation of the surface by the solid, and if the solids are insoluble in water they are best cooled by water sprays.

Dryers, evaporators, and stills all require condensing systems.

Surface condensers operate on exactly the same principle as the Liebig condenser in the laboratory. Vapors ordinarily pass through coils or tubes connected with common headers, and water surrounds the coils or tubes. In the manufactured-gas industry, water may be passed through the tubes, and the gas from which a limited amount of vapor

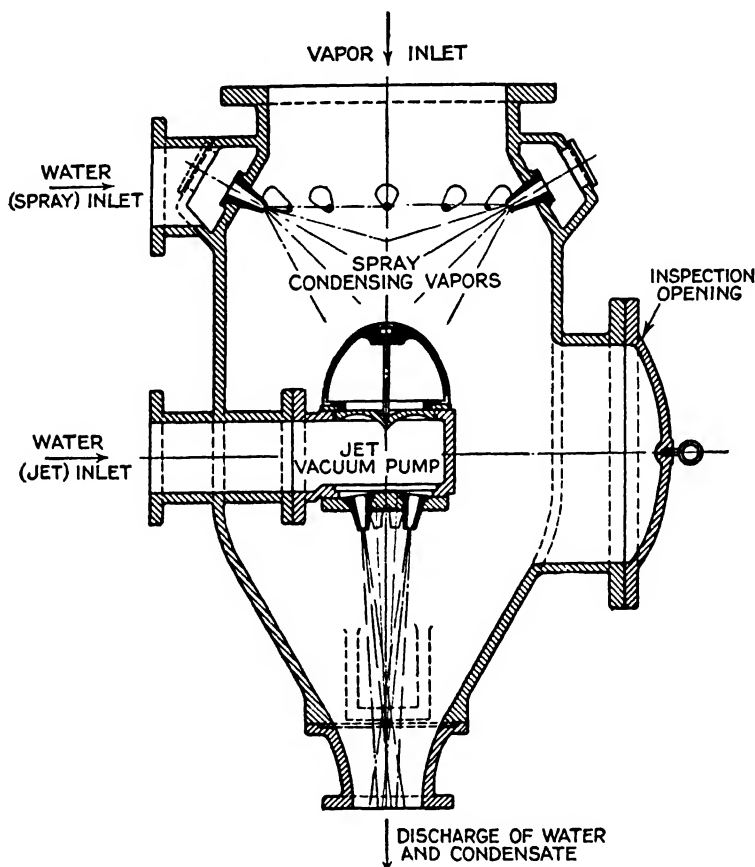


FIG. 52.—Barometric Condenser with Jet Vacuum Pump Courtesy
• Schutte and Koerting, Philadelphia, Pa.

is to be condensed surrounds the tubes. Heat exchangers also often function as surface condensers, and are generally concentric tubes with counter-current flow.

Steam which is not to be recovered is condensed by direct contact with the cooling water. By means of jets both cooling and production of a vacuum are simultaneously attained. When such condensers are

equipped with a long vertical discharge pipe terminating in a small open reservoir called a "hot well," they are known as "barometric" condensers. If a barometric leg is not used, the water must be removed by a pump. The same pump may serve to remove uncondensed gases, condensate, and cooling water, or two pumps may be used, one for gases and the other for fluids.

7. PRESSING

Liquids are also separated from solids by pressing, this being limited largely to cellular, fibrous, or otherwise highly absorbent mate-

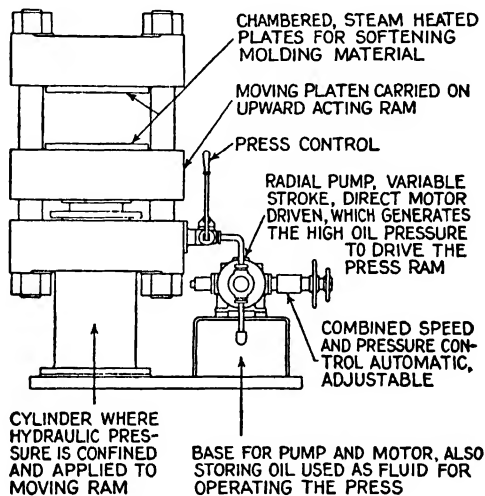


FIG. 53.—Hyro Power Plastic Molding Press. Courtesy The Hydraulic Press Manufacturing Company, Mount Gilead, Ohio.

rials, as seed meals and fruit pulps. Hydraulic presses are made up of a cylinder in which very high hydraulic pressures are exerted upon a moving piston or ram, a platen on the upper end of the piston, and a heavy frame attached at its base to the cylinder and at its top to a fixed plate. The material to be pressed is placed between the platen and the upper fixed plate. In some cases the material is confined in a perforated cylinder within which the platen moves, and in others it is made into cakes, wrapped in press cloths, and laid on a tray supported by movable plates spaced by loose links. As the platen is forced up by the ram, very high pressure is applied, and the liquid is forced out from the cellular material and drains from each tray. Hydraulic presses are also used in molding operations, particularly in

the rubber and synthetic resin industries, the plates being equipped for heating.

A continuous pressing device is the Anderson expeller mill, which is extensively used in the vegetable oil industry. The seed meal is brought to the proper temperature by heating and stirring it in a "tempering" chamber. It is fed to the expeller by a screw conveyor and passes into a heavy horizontal pressing cylinder equipped with numerous small drainage openings. Within this moves a heavy worm

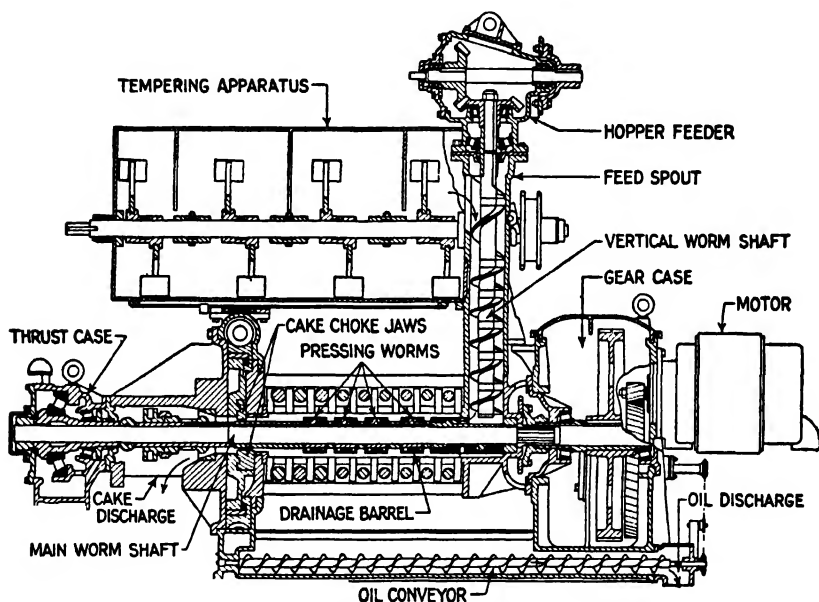


FIG. 54.—Anderson Expeller Mill. Courtesy V. D. Anderson Company, Cleveland, Ohio.

shaft. The material is forced along in the annular space between the cylinder and the shaft. At the discharge end the space is still further restricted by a "choke" mechanism. The forcing of the material by the worms against this restricted opening develops high pressure, and the liquid is forced from the fibrous solids, drains through slots in the cylinder, and is removed by a screw conveyor. The pressed solids in the form of a thin cake are discharged at the end of the cylinder.

Removal of liquids from fibrous solids is also illustrated by the rolls of the cane mills described in Chapter XXI in connection with cane sugar manufacture.

8. LEACHING AND DISSOLVING

The term "leaching" commonly refers to the removal by a liquid of soluble material from lumps of solids that remain in a fixed position. Dissolving is a term that assumes the material to be largely soluble and to be brought into intimate contact with the solvent by means of agitation. Very often, "extraction" is used to cover all such operations.

Open tanks with perforated or filtering bottoms and equipped for the passage of the solvent down through the charge are widely used, and are often called "Shanks tanks." When the material is of such a nature that the solvent diffuses through vegetable membranes, such as beet slices and wood chips, and must be forced through closed tanks under pressure, the equipment is called a "diffusion cell," and a series of such cells a "diffusion battery." When the material is coarsely granular, Dorr classifiers, ordinarily of the multiple deck type, are often used for extraction purposes.

Finely divided material is thoroughly agitated with a solvent for purposes of extracting soluble substances. A Pachuca tank is a vertical cylinder with a large central pipe equipped with air stirrers. The suspension of solids is carried up through the inner pipe in which air agitation is very thorough, and the solids settle slowly in the quiet outer space. The Dorr agitator has already been described, and is extensively used for extraction of fine solids.

Dorr agitators and thickeners are often used together for continuous extraction; washing remaining solids free of adhering soluble material; and removing a thickened sludge. This process is referred to as "continuous counter-current decantation," and a typical instance is described in connection with the production of caustic soda (Chapter XIV).

9. ABSORPTION AND ADSORPTION

Chemical engineers use the general term "absorption" to describe the removal of a component of a gas by means of a liquid. When a substance is removed from a gas or liquid by means of a solid, and when the concentration of this substance on the surface of the solid is high in proportion to its concentration in the fluid, "adsorption" is the term employed.

It is necessary to bring the absorbing liquid into intimate and thorough contact with the gas from which a certain component is to be removed. When the material is extremely soluble, tourills, Woulfe bottles, and fused silica S bends may be used, as in the removal of

hydrogen chloride from the pan, roaster, or mechanical furnace gases of the hydrochloric acid process. The absorbing liquid may be sprayed through the gas, this being illustrated by the Bartlett Hayward washer, used in the manufactured-gas industry. In this washer, concentric sections of inverted cones rotate in a compartment partially filled with liquid, and throw a spray into the gas space. There are several superimposed compartments, the liquid and gas passing counter-current through them. Rapidly rotating disks on which liquid is poured serve the same purpose of producing a spray.

The most common and widely used method of absorption is to run the liquid down a tower packed with quartz, stoneware shapes, or similar distributing material, and to pass the gas up through the tower. Bubbling plate columns are used for this purpose in the Solvay soda process. The use of towers for absorption will be referred to repeatedly in later chapters.

Such materials as silica gel and activated charcoal are employed to adsorb condensible hydrocarbons from gases. The hydrocarbons are recovered by the use of steam. The adsorbing solids are either placed in a series of adsorbers, or a single large unit is used, which is regenerated when it has reached the limit of its capacity.

10. CHEMICAL

In the chemical industry a considerable number of typical chemical operations require special equipment, which cannot be described in this chapter. Aromatic hydrocarbons are treated with mixed acid (nitric and sulfuric acids) for purposes of nitration, and the equipment must be provided with simple stirring and cooling devices. The equipment in which sulfonation takes place is so arranged that thorough stirring and application of heat, both in jackets and in closed-end tubes, is easily done. Reduction of nitrobenzene by the use of iron filings in the presence of hydrochloric acid requires a closed vessel with scrapers, discharge opening of ample size, and reflux condensers. Caustic fusion is carried out in closed pots and kettles. Autoclaves are provided with stirrers and heating devices, and operate under pressures that are sometimes quite high. The whole field of high-pressure reactions includes many special types of equipment, developed for very highly specialized purposes.

In general, however, the larger part of manufacturing operations that involve physical and chemical changes are carried out in standard equipment that may be classified under one of the first nine headings of this chapter.

CHAPTER VIII

MATERIALS OF CONSTRUCTION

The first factor in determining the choice of materials of construction of plant equipment is that of resistance to corrosion, and the second is whether or not it can be worked into suitable form. If satisfactory in these two respects, the next factor is the cost. A number of considerations enter into cost determinations. If the process is likely to be used over a very long period of time, first cost of highly resistant material may be high and depreciation and replacement costs low. If it is likely that the process will be supplanted shortly, a cheaper material may be chosen, and periodically replaced at points of greatest wear. In its wearing or dissolving it must not seriously contaminate the product. The material itself may be cheap, but its cost of fabrication may be high, or it may possess inadequate mechanical strength. Mechanical strength was once by no means so important as in this era of very high pressures. Temperatures are often much higher, and frequently there is a demand for a material with adequate mechanical strength and resistance to wear and corrosion at high temperatures and high pressures. Corrosion in most cases is much more severe at higher temperatures. Even though a piece of equipment can be repaired readily, there is the expense and inconvenience of stopping production or overhead on standby equipment.

Nothing short of actual use over a long period of time under all the variations of plant operation will determine ultimate usefulness. A material that successfully passes laboratory tests may fail entirely in use in the plant, by reason of some factor that was either overlooked or could not be duplicated. Corrosion is a function of exposed surface, and there is little relation between turnings or test strips in a beaker and the surface of a tank, pump, or pipe. Under certain conditions, particularly in the presence of strong oxidizing agents such as chromic acid and nitric acid, and even sulfuric acid, iron becomes "passive." Protective coatings of insoluble compounds are often formed that resist chemical action, but these may be removed by sudden temperature changes, or more commonly by erosion of rapidly

flowing liquids. There is a distinct difference between uniform corrosion and pitting. There may be comparatively little total loss, but a single hole often renders the whole equipment worthless as well as constituting a source of loss and danger. Pitting may take place under plant conditions, although laboratory tests show no indication of it. The composition of raw material may change slightly, and a small amount of an impurity may be introduced that will entirely alter the effect on the container.

In general, very concentrated aqueous solutions are less corrosive than those more dilute; but there are exceptions to this rule, the most notable being where molecular complexes are formed. Not only are higher temperatures more likely to produce corrosion from solutions, but there seems to be a certain temperature above which the rate of solution increases very sharply. Inhibitors, which are commonly bases or positively charged colloids, have been developed, and serve to diminish or prevent the attack of acids on metals. In general, they do not greatly affect the action of acid on oxides or salts. These substances go to the cathode along with hydrogen. Since they cannot escape by gaseous evolution when discharged, they are adsorbed and build up a protective layer.

It cannot be said that there is any one theory of corrosion that applies alike to all cases, since there are different factors for every material of construction and every product that is handled. Battery action due to dissimilar metals improperly insulated and dipping into a conducting solution, stray currents, or the presence of such active metals that no insulation will prevent their solution and the deposition of less active metals upon them are obvious sources of corrosion. The presence of segregated impurities in the metal or deposition of products of corrosion and development of potentials between them and the main body of metal are known to cause corrosion. It is also essential to know the strain to which the metal is subjected while in contact with corrosive substances. The whole problem is a broad one and has many variations.

Materials may be classified broadly into:

- I. Metals and their Alloys.
- II. Inorganic Non-metals.
- III. Organic Substances.

It is also necessary to distinguish between materials used as protective coatings for others, and those which are the sole material of which the equipment is fabricated.

I. METALS AND THEIR ALLOYS

Iron. What is technically known as *pure iron* is a product which contains not more than 0.15% of substances other than iron. It has a limited use in chemical industry, being particularly resistant to dry hydrogen chloride gas. *Wrought iron* comes next in point of purity, and is resistant to caustic soda and to "mixed acid" if the amount of water is less than 20%. This material is used more largely in piping than in any other form. *Cast iron* is a term which includes a very considerable variety of alloys of iron. The ordinary product of the iron industry has as much as about 4% of its chief alloying component, carbon, and smaller amounts of silicon, phosphorus, sulfur, manganese, and traces of other elements. The form in which carbon is present, whether as carbide or as graphite, is important. Chemical industry employs a great deal of cast iron in the fabrication of equipment, but its use is limited to operations where pressures are low or where no pressure is developed. When a cast iron vessel bursts, it breaks into many fragments. Failure of cast iron to meet requirements is probably as often a matter of foundry defects as it is lack of ability to withstand corrosion, shock, and mechanical strain. Cast iron resists sulfuric acid above 80%, but is disintegrated by oleum. It can be used with anhydrous ammonia, with caustic soda solutions, and with dry hydrogen chloride. There is apparently a growing tendency on the part of chemical industry to set up certain specifications for cast iron, particularly that it shall contain small amounts of nickel and chromium to give higher resistance to wear. The low alloyed cast irons are rapidly increasing in importance in the process industries. Corrosion-resisting cast iron has from 1% to 3% nickel and from 0.3% to 0.9% chromium. The limiting factor in the amount of these alloying materials is the difficulty of machining the product. These two elements are used in improving resistance to wear and corrosion; molybdenum has the same effect but to a lesser extent. Strength is attained by a proper balance of nickel, silicon, and manganese. *Steel*, particularly those alloys low in carbon known as "mild steel," finds very wide and extensive use in chemical industry wherever considerable mechanical strength and resistance to impact and shock are requirements. Even where there is a certain amount of corrosion and resulting replacement, it is common practice to use steel. Small amounts of copper are added to steel to insure its life under severe conditions of use. Vanadium in mild steel increases the resistance where corrosion conditions are not exceptionally severe. If a very high resistance to acids of varied concentration is needed, *silicon-iron alloys* are very

widely used. Such alloys may be employed with cold hydrochloric acid, and with nitric and sulfuric acids, hot or cold. The optimum percentage of silicon is around 14.5%. Although the mechanical properties of these alloys have been considerably improved in recent years, they are still somewhat brittle, and unless care is taken in keeping down length of individual sections, damage may result by rapid temperature changes. They cannot be machined, and thus must be cast and ground to the desired form, but they can be welded by the oxyacetylene flame. In recent years, several iron alloys have been developed that are highly resistant to chemical action at high temperatures, withstand abrasion, and retain mechanical strength at red heat. Which of these qualities predominates in a given alloy depends on its composition. Their introduction into chemical industry has made possible a number of new processes. The combination of high temperature and high pressure bids fair to revolutionize several important industries. Chief among these materials are *chromium-iron alloys* and *chromium-nickel-iron alloys*. The terms "stainless irons" and "stainless steels" are unfortunate when applied to these alloys as they are used in the chemical industry. It is better to designate them as "heat-resisting" or "corrosion-resisting" rather than as "stainless," a trade name applicable only to chromium-iron alloys. Their resistance to abrasion increases with increasing carbon content. The resistance to corrosion of various alloys is not always the same with different acids. An iron alloy containing chromium is highly resistant to nitric acid, but in a number of other cases is less resistant than the iron-chromium-nickel alloy containing 18% chromium and 8% nickel. Unless the chromium content is very high, these alloys may be successfully welded. All such alloys must be heat treated to permit fabrication. It is of extreme importance to obtain the solid solution type of structure. Silicon may be used with alloys of this type in amounts up to 3%, without brittleness. Still higher amounts of silicon increase corrosion resistance. An alloy of 5% silicon and 25% nickel is said to resist the action of dilute sulfuric acid at the boiling point even in the presence of ferric sulfate. *Nickel-molybdenum-iron* alloys, which are cast in fabrication, are more resistant to hydrochloric acid, both anhydrous and aqueous, than most other alloys.

Both ordinary steel and the newer heat- and corrosion-resisting alloys, when used in high-pressure equipment, are now fabricated largely by welding instead of riveting. In these cases, welding must be done with great care to preserve chemical homogeneity within the sheet. Aside from heads, manhole lids, stuffing boxes for stirrers, and

the like, the whole piece of equipment is essentially continuous metal. Such equipment is subjected to severe tests, and an occasional unit is deliberately stressed to the point where it fails in order to study the way in which failure may take place. Needless to say, the strains of use are kept far below those under which failure occurred.

Copper. The greatest single use of copper is as a conductor of electric current, but this has a limited significance in chemical industries. In addition to high heat conductivity, copper resists the action of dilute organic acids, and is thus very generally used in the alcohol and sugar industries. It is peculiarly subject to oxidation, however, and the oxides dissolve readily in acids. Copper resists the action of concentrated caustic soda (40% and over) better than steel. The quality of copper may be improved by deoxidation, phosphorus being the most efficient means of oxygen removal. The two main types of copper alloys may be classified as *brasses* and *bronzes*, the former being mainly a zinc-copper alloy and the latter containing tin. These terms are used somewhat loosely, particularly "bronze," which may refer to alloys containing manganese or aluminum. Likewise brasses usually contain other elements than copper and zinc. Recently a number of valuable alloys in which copper is the predominating element have been developed, each of which bears a distinguishing trade name. In these, aluminum, nickel, manganese, and silicon are used, the number and amounts of these elements being subject to a considerable variation. Some require special heat treatment before use. Silicon is particularly valuable in rendering copper alloys resistant to corrosion, and certain of these alloys are also quite workable.

Lead. Comparatively pure lead is quite soft, has little mechanical strength, and must be reinforced at a number of points to insure its retaining shape. It has a very low melting point. On the other hand, it is most easily fabricated by the use of a simple gas-oxygen torch, and patching and repairing are very conveniently done. Lead is particularly useful in handling sulfuric acids of all concentrations up to 96% when cold, and even hot acid up to 77%. Alloying lead increases its susceptibility to chemical action, and small amounts of impurities may render it quite unfit for special uses. Lead is most commonly alloyed with antimony; what is known as "hard lead," a material of considerable mechanical strength, contains around 12% antimony. Lead may be bonded to steel either by the use of solder or by careful fluxing.

Nickel. The chief uses of technically pure nickel are in the food industries, where it successfully resists fruit acids; in the evaporation

of caustic soda solutions; and in caustic fusions where traces of iron are to be avoided. In addition to equipment made of solid nickel, this metal finds extensive use as a protective coating for steel. "Nickel-clad" plates are made of mild steel and malleable nickel. Usually the steel constitutes 90% of the thickness and the nickel only 10%. Owing to the solubility of iron and nickel at rolling temperatures, the process of manufacture in use effects a perfect bond between the two metals. This offers the advantages of the protective properties of nickel and the strength and weight of steel plate. The *copper-nickel alloy* known as "Monel metal" resists the action of dilute sulfuric acid, and also finds many other uses in chemical industry. It is commonly rated between nickel and copper in its general usefulness.

Aluminum. The light metal aluminum is available in a high degree of purity, 99% being regarded as the minimum for a technically pure product. It resists organic acids and its salts are non-poisonous, hence it finds extensive use in the food industries. Pure nitric acid does not attack it, but in the presence of sulfuric acid and the oxides of nitrogen in solution it is corroded. Aluminum is uniquely susceptible to hydrochloric acid even in minute amounts. It is easily fabricated, being readily wrought or cast. It is particularly valuable in resisting the action of sulfur and sulfides, especially in the petroleum industry. Small amounts of alloying materials may be used with this metal. Silicon improves its casting properties, and manganese up to 1.25% is also employed.

Chromium. In addition to being of great value as a component of heat and corrosion-resisting iron alloys, and in connection with cobalt and tungsten in another series of valuable materials, chromium itself stands wear, high temperatures, and some very severe corrosion conditions such as the action of sulfur and sulfur compounds. Being comparatively expensive it is used mainly as a protective coating for other metals. It is readily applied by electroplating.

Zinc and Tin. These metals are mainly employed as protective coatings. Zinc is applied by dipping, spraying, or as a vapor, a process called "sherardizing." It owes its protective value both to the fact that it forms in the air a basic carbonate, which is quite adherent, and to its position in the electromotive series with reference to other structural metals, particularly iron. Tin is valuable in handling distilled water even when it carries carbon dioxide, but has its greatest use in coating thin sheet iron for food containers. Tin has the disadvantage of being lower in the electromotive series than iron, and theoretically when its surface is broken so that both metals are in contact with a

conducting solution it stimulates corrosion. However, it has been shown that in contact with certain vegetable and fruit acids tin is slightly more electropositive than iron.

Other Metals. A number of other metals are of importance in this field. Cadmium plated on steel is highly resistant to the action of certain chemicals such as calcium chloride. The greatly lowered price of silver makes this available for a number of purposes. Tantalum costs about one-fourth as much as gold, but it is of extreme hardness and is inert to all chemical reagents except hydrofluoric acid, fused caustic soda, and 95% sulfuric acid at boiling temperatures. It may be electroplated on other metals and spot welded to iron and steel. It is peculiarly adapted to use in rayon spinnerets. Gold, platinum, and other metals related to them and generally known as "precious metals," though not used in great quantities, play a very significant part in the success of many industries. As contact points, thermocouples, resistors for development of very high temperatures, spinnerets, catalysts, and as protective coatings, these metals often function where no other material could.

Before leaving the field of metal surfaces, it should be noted that in addition to coating one metal with another more resistant metal by spraying, dipping, welding, rolling, and electroplating, it is possible to alter the nature of the surface by diffusion of one substance into another. Aluminum may be made to penetrate into the surface of steel and thus render it more resistant to oxidation at high temperatures. The process of nitriding consists in heating a metal with nitrogen compounds with the formation of nitrides, which resist both abrasion and corrosion. Iron phosphate on the surface of steel gives it greater life when exposed to ordinary weather conditions.

II. NON-METALLIC INORGANIC MATERIALS

While metals in general have the desirable properties of mechanical strength and high heat conductivity, there are certain conditions in the chemical industry in which non-metallic inorganic compounds compete on an even basis, and still others where they must be used exclusively.

Glass. There are several characteristics which make the highest grade of chemical glass a most valuable material for the chemical industry. Transparency is a minor consideration. The newer borosilicate glasses, known as Pyrex, have a low coefficient of expansion, their softening point is quite high, they are easily formed into practically any desired shape, and their hardness and resistance to chemical

action make them invaluable. By the use of rubber gaskets and sleeves it is possible to make connections satisfactorily. The heat conductivity of glass is much less than that of metals, but its polished surface gives it decided advantage over an oxide-coated metal in connection with radiant heat. In addition to laboratory glassware, glass is now found in condenser tubes, heat exchangers for liquids, and even in bubbling columns for stills. The action of hydrofluoric acid, hot concentrated phosphoric acid, and alkalis on glass constitutes its main chemical limitation.

Fused Silica. Though considerably more expensive than glass because of the higher cost of production, fused silica is more resistant to high temperatures and sudden changes of temperature. It has a very low coefficient of expansion and very high softening and melting points, and is safe in service up to 1100°C . It has in general the same resistance to chemical action as glass. Fused silica finds considerable use in cascade concentrators, condensers and absorbers for nitric and hydrochloric acids, and in stills for fine chemicals. Clear fused silica is permeable to ultraviolet light.

Chemical Stoneware. Chemical stoneware resembles porcelain in its general nature, but has a decided color, a lower vitrification point, and greater mechanical strength before firing. Every piece is made to order according to definite specifications. By very accurate control of shrinkage it is possible to make various parts fit each other. Chemical stoneware can be machined and polished. It has a surface glaze to permit ready cleaning, but it is throughout of a dense and impervious nature. A surprising number of different types of chemical equipment may be made of chemical stoneware. It is used primarily with acids, other than hydrofluoric, of all concentrations, and is particularly valuable with hydrochloric acid and chlorine.

Acid-Proof Brick. The ceramic industry has developed a brick highly resistant to the action of acids and corrosive gases even at high temperatures. This brick appears not only in conventional form, but with radial curvature for lining cylindrical vessels, and in special shapes for tower packing, the most common forms being rings and spirals. Acid-proof masonry finds considerable use in the towers of the lead chamber process of sulfuric acid manufacture. Acid-proof cements are used as a setting for such brick in lining vessels.

Refractories. A considerable variety of refractories are available to the chemical engineer. For certain specialized uses, silicon carbide is necessary. Aluminum oxide, made by electric furnace process, has a limited use in small-scale equipment. Porcelain is the material of

pots for melting optical glass. The most widely used of all refractories is firebrick, which is employed in furnace linings, flues, recuperators, regenerators, and wherever very high temperatures are encountered.

Heat-Insulating Materials. Magnesia and asbestos are the most common heat-insulating materials. Naturally occurring minerals, largely silica, which represent the skeletal remains of very minute forms of animal life and which are classed together under the name "diatomaceous earth," are very valuable for heat insulation, either finely divided and loosely packed between retaining walls, or cut and pressed into the form of brick. They are also used in cements, and to improve the "workability" of concrete. Calcined alumina, made from bauxite or hydrated alumina, has very low heat conductivity and maintains this resistance to heat flow up to 1900° F. It can be made into large blocks for use in installations of considerable size. In the field of insulation at low temperatures, that is for brine and ammonia lines, cork is a most valuable material.

Ceramic Protective Coatings. Certain cements resistant to the action of most substances may be used as a protective lining for metal reaction vessels, an example being the soaking drums in petroleum-cracking units. Enamels are essentially glasses, usually carrying substances that give them opacity and generally a definite color. The chief objection to enameled-iron equipment has been the ease of breakage and the fact that a single fracture of the surface, even a small one, which permits access of the corrosive liquid to the metal, renders the whole equipment useless. This has been met to a considerable extent by building such equipment of standard parts with readily removable liners. Heating of enameled metal must ordinarily be indirect. There are, however, instances of enameled tubes in economizers, where the action of sulfuric acid from the sulfur of the fuel must be prevented, which are capable of withstanding sudden changes of considerable magnitude, and which can readily be patched.

Carbon. Because of its great chemical inertness, carbon is finding many uses in chemical industry in addition to its use as a refractory and a resistor in the development of high temperatures in electric furnaces. In the pyrolytic process for phosphoric acid and the contact sulfuric acid process it is indispensable. It is being tested with considerable success for use in digester linings. Because of its low coefficient of friction it is being employed in rings connecting the steam-heated dryers and as the material of the tops of suction boxes in paper machines.

III. ORGANIC MATERIALS

It is obvious that organic materials are limited to use at relatively low temperatures. In general they lack mechanical strength, and some of them are acted upon by organic solvents.

Wood. To a limited extent, wood is used in tanks for dilute solutions, such tanks being generally unlined, though for some purposes lead and soft rubber are used as protective inner coatings. An important use of wood is in the plates and frames of filter presses in which dilute acids are handled. Cypress and maple are regarded as superior for water storage, since pine and fir give taste, and oak and redwood a color to the water. Wood may be impregnated with zinc chloride, and wood so treated is used extensively in the paper and textile industries.

Cloth. A very considerable amount of fabric is used in chemical equipment in the form of filter cloth for filter presses and leaf and drum filters. Very fine cloth has some use in screens, though most screens are woven wire. Hydraulic press cloths are often made of woven animal hair. Cellulose nitrate in the form of fabric may be used in filtering nitric acid solutions.

Resins and Plastics. The most widely used plastics are those of the phenol-formaldehyde type. In order to secure mechanical strength, cellulosic and mineral fibers are incorporated before they are molded and hardened. Although susceptible to strong acids and alkalis in considerable concentrations, these materials resist weak acids, hot water, and steam. They are especially valuable as materials of gears, or as a coating on steel gears that are exposed to corrosive liquids. The largest use of these synthetic resins is in the form of electrical insulation.

Rubber. Soft rubber is most largely used as a lining of tank cars and storage tanks. Wooden tanks lined with rubber have already been referred to. In recent years soft rubber has been vulcanized to steel. All the advantages of the high chemical resistivity and permanence of rubber are obtained, together with the high mechanical strength of steel. Soft rubber withstands abrasion many times as well as steel, and thus finds use in lining ball mills, particularly for wet grinding. Since the balls are of silicate materials, metallic contamination is prevented. Pipes lined with hard or soft rubber, and pipes and valves made entirely of hard rubber, are used very largely in connection with hydrochloric acid, and are especially useful in handling hydrofluoric acid. Hard rubber also resists the action of sulfuric acid up to 50° Bé

material, solutions of phosphoric acid up to 75%, and caustic soda solutions. It is softened and swelled by a number of organic liquids, particularly benzol and similar aromatic hydrocarbons, aniline, carbon bisulfide, and chloroform.

Protective Paints. Ordinary paints are compounded of a moderately volatile solvent, drying oils, resins, and inert pigments. Red lead is a standard pigment for the first coat on structural steel. Lacquers are solutions of cellulose nitrate carrying pigments and plasticizers. Powdered aluminum is a widely used pigment, both for the outer jackets of insulated vessels to prevent excessive radiation, and for tanks holding volatile liquids to cut down radiant heat absorption. Bituminous paints are standard protective coatings of metal and concrete where conditions make their use possible, being specially valuable in withstanding the action of weather corrosion.

CHAPTER IX

CHEMICAL ENGINEERING UNITS AND CALCULATIONS

The engineering profession as a whole in the United States unfortunately has not adopted the metric system, and still holds to the Fahrenheit temperature scale. For this reason the units of measurement referred to in this text need some explanation. There is a growing conviction on the part of engineers that the metric system should be adopted. The change necessarily must be gradual, but if engineering graduates already familiar with metric units will use these units wherever possible and make every effort to secure their adoption in their own plants, the change to the more sensible and convenient system can be secured in much shorter time. It is also the purpose of this chapter to describe very briefly the general types of calculations made by chemical engineers. This will be done without the use of data and examples, all of which would involve more space than is in keeping with the general nature of this text.

The units of weight are the pound and the short ton; those of volume, the United States gallon for liquids and the cubic foot for solids; and for length, feet and inches. The unit of volume for gases is commonly the cubic foot, but where large volumes are dealt with the unit is 1000 cu. ft. When the Fahrenheit temperature scale is used, absolute zero is -460°F. , and thus absolute temperatures, often referred to as "degrees Rankine" ($^{\circ}\text{R.}$), are obtained by adding 460 algebraically to the Fahrenheit value. The gas constant, R , when pressures are in pounds per square foot, volumes in cubic feet, and temperatures in the Rankine scale, is 1543. Obviously, n , or the number of mols or the mol fraction, of the formula $PV=nRT$ must be in terms of pound mols. The pound molecular volume is 359 cu. ft., in the same way that the gram molecular volume is 22.4 liters.

Thermochemical data in laboratory work and theoretical investigations are commonly in terms of calories, a calorie being the quantity of heat that will raise one gram of water at its maximum density one degree Centigrade, or from 3.5°C. to 4.5°C. In Europe, engineering

calculations are ordinarily in the large calorie or kilogram calorie, which is 1000 small calories, or the quantity of heat that will raise one kilogram of water one degree Centigrade. The joule is also a unit frequently used in theoretical work. If both Fahrenheit degrees and pounds are used, the heat unit is the "British thermal unit," or B.t.u., which is the quantity of heat that will raise one pound of water one degree Fahrenheit. Chemical engineers break away from tradition far enough to use the "Centigrade heat unit," or C.h.u., which is the quantity of heat that will raise one pound of water one degree Centigrade. Since thermochemical data in the scientific literature are in calories, and since the ratio between grams of substances used in a reaction and grams of water heated is the same as that of pounds of substance and pounds of water heated, such data may be used directly as C.h.u., and converted to B.t.u. if desired by multiplying by 1.8. One B.t.u. is equal to 252 gram calories, but one gram calorie per gram equals 1.8 B.t.u. per pound.

Specific gravities in the laboratory are weight ratios of unit volumes of a solid or a liquid to the same unit volume of water, the temperature of the material in question and that of water being stated. The most widely used reference temperature is 15° C. for both, but in many cases other temperatures are used. In handbooks the usual method is to write the temperatures of the material above a line and that of water below the line, for example, 20°/15°. Gases are usually compared with air, this being regarded as having an average molecular weight of 28.97, or roughly 29.0. There are several scales of specific gravity used in industry, the most common being the Baumé scales for liquids lighter and heavier than water. These scales were developed by means of water and salt solutions at 60° F. The details of the origin of the Baumé scales are given by Leighou in "Chemistry of Engineering Materials." The formula for conversion used for liquids lighter than water by the Bureau of Standards is

$$\text{Degrees Baumé} = \frac{140}{\text{Specific Gravity}} - 130$$

The petroleum industry uses a different specific gravity scale that has been adopted by the American Petroleum Institute. The relation between the water ratio value and this scale is as follows:

$$\text{Degrees A.P.I.} = \frac{141.5}{\text{Specific Gravity}} - 131.5$$

Liquids heavier than water use another Baumé scale, the commonly used conversion formula being

$$\text{Degrees Baumé} = 145 - \frac{145}{\text{Specific Gravity}}$$

On the lighter-than-water Baumé scale, water is 10° Bé, and on the heavier-than-water scale it is 0° Bé. Thus a 66° Bé gasoline has a specific gravity of 0.7144, a 66° A.P.I. material a specific gravity of 0.7164, and 66° Bé sulfuric acid a specific gravity of 1.8354. Corrections for temperature vary for each liquid, and such data are available in commercial handbooks. The sugar industry uses the Brix scale, which is in terms of per cent apparent solids. Other specific gravity scales, such as the Twaddell, are used in England to some extent, but only the two described are in use in this country.

The standard barometric pressure in laboratory measurements is in millimeters of mercury, the sea-level value being universally considered to be that pressure that will force pure mercury at 0° C. into a vacuum to a vertical height of 760 mm. Low pressures are thus recorded in millimeters of mercury, and higher pressure in terms of atmospheres, or multiples of the 760 mm. value. In terms of weight per unit area this is 1033 grams per square centimeter. In chemical engineering the barometer is read in inches of mercury, the standard being taken as 29.91 in. Very low pressures in industry are reported in millimeters of mercury as absolute pressures, or the vertical distance the gas in a vessel would force mercury into an empty space. Ordinary pressures are expressed in pounds per square inch, atmospheric pressure being taken at 14.7 lb. per square inch. It should be noted in calculations that gauge pressures must be increased by 14.7 lb. in order to get absolute pressure. In dealing with reduced pressures, the common dial gauge records the inches of mercury difference between the absolute pressure and one atmosphere. Thus a 26-in. vacuum means an absolute pressure of $29.91 - 26.0 = 3.91$ in. of mercury, which is equivalent to 99 mm. of mercury. The simple gas laws may be used with a fair degree of precision with gases at low pressures and high temperatures. Under reversed conditions, high pressures and low temperatures, there are very considerable deviations from the simple gas laws. Calculations under these conditions involve knowledge of the critical state, compressibility factors, certain equations of state, as well as the use of empirical methods.

There are two general types of calculations with which chemical engineers are concerned: (a) those which deal with quantities used

and produced by chemical change, or stoichiometrical relations; and (b) engineering calculations of power, quantities of solids, liquids, and gases handled, the flow of heat, and the amount of material entering into such physical changes as evaporation or drying. Stoichiometry has all the exactness of atomic and combining weights, whereas the calculations concerning flow of heat and of materials are in many cases approximations because of inadequate formulas and similar inevitable and inherent difficulties. A great deal of fundamental physical research still needs to be done in order to provide the chemical engineer with data on which to base calculations, and it should be done by physical chemists in university laboratories.

For complete discussion of these topics the reader is referred to the following books:

“Industrial Stoichiometry” by Lewis and Radasch.

“Industrial Chemical Calculations” by Hougen and Watson.

“Elements of Chemical Engineering” by Badger and McCabe.

“Principles of Chemical Engineering” by Walker, Lewis, and McAdams.

“Chemical Engineering” by Olsen.

This chapter is largely a very brief summary prepared on the basis of what is contained in these books.

Practically all chemical engineering operations involve fuels, either for the production of heat energy or power. All types of fuels can be evaluated with considerable precision as regards the quantity of heat they will produce. The main combustible substances in a fuel are carbon-hydrogen compounds. In some fuels, sulfur is present in such amounts that it cannot be neglected. Nitrogen in fuel, either free in gases or combined in solids and liquids, appears in the fuel gas as nitrogen, and if present in amounts greater than 1%, or 2% at the most, must be allowed for. The data necessary in calculations involving fuels and combustion include: analysis of the fuel (preferably ultimate, but for solid fuels carbon and hydrogen may be obtained with fair accuracy from a proximate analysis); determination of the calorific value of the fuel; analysis of flue gases; measurement of their temperature; and tests of the ash to determine unburned combustible matter. On the basis of such data it is possible to calculate the amount of air used to furnish oxygen for combustion; the amount of excess air; the amount of unburned fuel; the quantity of gases that enter the stack; the heat losses due to sensible heat of stack gases, to formation of carbon monoxide instead of dioxide, to vaporizing water formed in combustion, and unburned fuel; the amount of heat recover-

able from stack gases; and preheating of gaseous fuels that can be accomplished by hot waste gases. All these calculations are based on combining proportions by weight and volume, the heats of reaction and vaporization, and molal heat capacities, and do not take into account the matter of film resistances. The calculations necessary for the proper operation of gas producers are very much the same as those for kilns and furnaces. Since the composition of air is practically constant, the nitrogen and the free and combined oxygen in the flue gas, after due allowance for nitrogen in the fuel, may be used to determine how much air has been admitted. On this basis and that of the volume relations of gas reactions, it is possible to estimate volumes of gases. Where the fuel is essentially carbon or carbon and hydrogen, practically all necessary information can be gained from a knowledge of the composition of the flue gas and the rate of fuel consumption.

The production of quicklime and of cement involves the combustion of fuels and chemical changes in the materials. The stack gases represent not only those resulting from the combustion of the fuel, but also those formed by the chemical decomposition of carbonates and complex hydrated silicates. Sulfur in the fuel is only partially accounted for in the stack gases, owing to complete oxidation of a part of it and combination of the resulting sulfur trioxide with the basic oxides of the kiln charge. With these modifications, the calculations are very much the same as those of ordinary furnace operation.

Closely akin to the burning of carbon compounds are those processes in which sulfur is burned and the sulfur dioxide converted to various compounds such as sulfates, sulfites, acid sulfites, sulfurous acid, sulfur trioxide, and sulfuric acid. The composition of the crude sulfur or the pyrites burned and the composition of the flue gases will tell how much sulfur has been oxidized to sulfur dioxide and how much to sulfur trioxide. In the manufacture of bisulfite-sulfurous acid solutions used in the paper industry, the formation of sulfates, either by oxidation of sulfur to sulfur trioxide during burning, or the oxidation of tetravalent sulfur in solution, represents a loss as far as efficiency goes, and the extent of this loss must be known and largely minimized by better methods of operation.

In the same way, the data obtained by analyses of sulfur-bearing material, burner gas, gases from the towers, and the nitrogen trioxide content of the acid circulated, and measurement of daily production, together with a knowledge of the humidity of the air entering the process, enable the chemical engineer to follow very closely the performance of a lead chamber sulfuric acid plant.

In general, two important economic considerations in industrial chemical operations are quantities of materials and quantities of heat. In order to keep up properly with these values in a process, complete weight and heat balances are necessary. A typical heat balance of a coal-fired boiler furnace is mainly concerned with the heating value of the coal as the major input value (over 99%). For very exact work, the heat content of the water vapor in the air is considered as input. It includes as output the heating value of the carbon monoxide, sensible heat of dry gases, heat content of water vapor, heat value of combustible in the ash, heat losses by radiation, and the heat which has gone into making steam.

In a chamber sulfuric acid plant the weight balance includes as input dry ore, dry air, and spray water, and as output the acid produced, dry spent gases, and cinder. The heat balance includes as input the heat of combustion of pyrite, and the heats of formation and solution of sulfuric acid and oxides of nitrogen as major factors. As output are the following: heats of radiation from burners and chambers, cooling of acid, and sensible heat of cinder, together with a number of minor factors, which together amount to not more than 3%, but which must be taken into account.

A very considerable body of data on reaction equilibria has been accumulated and is of very great industrial value. On the basis of the knowledge of equilibrium constants, the order of reaction involved, the effect of catalysts on reaction velocities, and the effects of temperatures and pressures, it is possible to determine equilibrium compositions of reaction mixtures and to calculate equilibrium reaction temperatures. Considerable progress can also be made towards deciding on optimum conditions even when equilibrium cannot be attained, which is usually the case in industrial operations.

A typical calculation in chemical engineering is that of solubilities of substances in various solvents, particularly those of crystallizable solids. Where the substance forms crystals that are free from combined solvents, the yields obtainable by crystallization are easily calculated from a knowledge of the degree of purity of the crude material and the solubility of the substance desired at the two temperatures employed. Where the solvent combines with the compound desired, as in the case of hydrate formation, the calculations are somewhat more complex. A very thorough study of equilibrium diagrams and phase rule relationships must precede operations in which several different substances are dealt with together.

Calculations on the rate of flow of fluids, both gases and liquids,

depend on the various pressures, in terms of heights of a column of liquid or "head," such as fluid head, pressure head, velocity head, and potential head; viscosities; whether or not the type of motion is turbulent or "straight line"; the shape and dimensions of conduits; and whether or not the flow, in the case of gases, is adiabatic or isothermal.

Heat flows by conduction, convection, and radiation. Most engineering calculations of heat conduction have to do with more than one kind of material, and generally with insulating of pipes, stills, furnaces, and other equipment to prevent undue heat losses. Such losses are in terms of B.t.u. per hour, and are determined by the use of dimensions of surface, thickness, temperature difference, and a constant of heat conductivity for each solid. Further temperature drops caused by incomplete contact involve additional losses, which must be experimentally determined by construction of small sections of the equipment to be used.

Convection applies to gases and liquids. In this case, the resistance to heat flow in the fluid is negligible, and the main portion of the problem has to do with stationary films. The more rapid and turbulent the flow of the fluid, the thinner the film, but the effect even with very thin films is large. This is due to the fact that heat can flow through the film only by conduction, and fluids are notoriously poor conductors. Equations for coefficients of heat transfer through films must be developed, and these differ according to the fluid and to the way in which it moves, that is, whether convection is natural or forced. Such film coefficients are in terms of "B.t.u. per hour per degree Fahrenheit drop through the film per square foot of film surface." Calculations must be checked by experiments in small scale, and a reasonable factor of safety in oversize equipment must be used.

Leaving out translucent bodies as without the field of chemical engineering, calculations of radiant heat are applied to bodies falling between the hypothetical highly polished surface, which reflects all the heat, and the ideal "black body," which absorbs it all. Most chemical engineering calculations of radiant heat are concerned with materials that are of the order of 90% "black." Hence, for substances of this nature, it is necessary to know the "black body percentage," the area, the temperature, and a constant known as the "black body radiation coefficient." The nature of the material radiating heat has no bearing on the problem. The energy is proportional to the fourth power of the absolute temperature, and for this reason radiant heat is of great importance wherever furnace temperatures are concerned.

No completely satisfactory expression has yet been developed for

the calculation of the energy required in crushing and grinding. One expression is based on the idea that the energy is proportional to fresh surface formed by subdivision; and another employs a coefficient obtained by experimental methods on the assumption that the "energy required for subdivision of a definite amount of material is the same for the same fractional reduction in average size of the individual particles." In regard to these expressions, Walker, Lewis, and McAdams say, "Neither equation represents the facts accurately, and it seems probable that a satisfactory expression, when it is developed, will lie between the two."

The separation of solids from liquids by settling involves the size of the particles, their specific gravity, and the viscosity of the liquid. Filtration is based on an understanding of the passage of liquids through capillaries, although the equation of Poiseuille is not directly used. Filtration calculations involve such determinable quantities as area of filtering surfaces, weight of filtrate and cake, pressure drops, resistances, and coefficients of compressibility.

Evaporator calculations require a knowledge of solubilities, temperatures, specific heats, heats of vaporization, vapor pressures, and coefficients of heat transfer. Since drying refers primarily to the removal of water from solids in the presence of air or other gases, it is always necessary to know the amount of water in the gas used, or the "humidity" of the gas. This also involves the saturation or dew point, and the heat required to raise the temperature of gases containing water vapor through a definite interval. Graphical methods are made use of to a great extent, particularly adiabatic cooling lines representing conditions when heat exchange with the surroundings is practically zero. The transfer of heat in drying must be considered in terms of temperature differences for unit times and volumes, and also requires the concepts of gaseous and liquid films. Other factors in drying calculations include the degree of shrinkage, the rate of diffusion within the body of the solid, and the formation of a "skin" on the surface, in which conditions are markedly different from those in the interior. As in many other engineering calculations, certain arbitrarily determined constants are used, which vary with the type of material and the kind of dryer used.

Calculations of yields in crystallization operations have already been discussed. The chemical engineer is also interested in the rate of crystal growth and the size distribution of the product as evidenced by a screen analysis. A common problem in crystallization is to add seed crystals to a saturated solution in order to produce larger crystals

of a predetermined size. On the basis of the screen analysis of seed crystals, the ratio of seed crystals to solution, and the solubility change of the material during the process, it is possible by use of graphic integral methods to calculate the screen analysis of the product.

Distillation of immiscible liquids requires only a knowledge of molecular weights and vapor pressure curves. Miscible liquids require data giving the vapor pressures and compositions of vapors at different temperatures. Binary mixtures which behave abnormally regarding volatility, and complex mixtures, will not be discussed. Even with binary mixtures of miscible liquids, there are marked deviations from Raoult's Law. Calculations involving partial condensation are largely graphical in their nature, and require the setting up of an equilibrium curve and an enrichment line; on the basis of this information it is possible to determine the minimum refluxing necessary in a column and the theoretical number of plates required. It is usually necessary to use more plates than theoretically indicated. Plate efficiencies of 100% can be obtained with properly operated bubble cap columns, but this is rarely attained in practice.

Absorption of the desired component in liquids, and adsorption on solid surfaces of such porosity that the surface is great in proportion to mass, constitute in general what are spoken of as "diffusional" processes. These include such operations as washing or scrubbing gases, adsorption of gases by activated charcoal, removal of volatile compounds from a liquid by a stream of gas, the extraction of substances from water solution by the use of an immiscible solvent by virtue of greatly increased solubility in the non-aqueous solvent, the decolorizing of solutions by percolation through various chars, and the extraction of solids by means of solvents. The "counter current" principle is commonly employed, in which the portion richest in extractable material is treated with the extracting agent containing already the largest amount of extracted substance, and that most nearly completely extracted with the most dilute extracting agent. In this way an equilibrium is continually approached. Chemical reactions, loose molecular complexes, and associated molecules are often involved. Once more the rate of diffusion and the concept of films must be considered. Many problems in this field are solved only by graphical integration.

It has obviously been impossible in this chapter to give illustrative data and examples. The whole aim has been to point out the nature and the limitations of chemical engineering calculations. Where chemical reactions are involved, stoichiometrical relations are very

exact and capable of accurate calculation. Processes that involve physical transformations and relationships constitute very complex problems, often involving simplifying assumptions, arbitrary and empirical constants, and large factors of safety. Much research yet remains to be done, but the application of the knowledge already gained has resulted in enormous savings and greatly increased efficiency in chemical engineering operations.

CHAPTER X

POWER PLANT CHEMISTRY

Steam plants are concerned first with the kind of water used in boilers. The composition and character of the fuel used to produce heat under the boilers are important. The performance of a steam power plant is rated on the basis of the composition of the flue gases. Gas and oil engine plants must depend upon the engineers' knowledge of the fuel used in the cylinders. Lubricants make possible the operation of all power plants, including hydroelectric installations. Hence an understanding of the chemistry and the chemical and physical tests made on water, fuel, and lubricants is necessary not only for the chemists and the chemical engineer, but also for all engineers who have to do with the production of power. Other very important chemical materials in the power plant are the refractories used in boiler furnaces and the metals of which modern boilers are made. These materials are referred to in other chapters, but it should be emphasized that the great advancements that have been made in steam power production have been largely due to the superior refractories and to the chromium-iron and nickel-chromium-iron alloys. Some of these alloys are used in grate bars because of their heat-resisting qualities, but they are of greatest value in the tubes and drums of the boiler, where high pressures and correspondingly high temperatures are possible only by the use of such remarkably strong and resistant materials.

BOILER FEED WATER

A complete analysis of a sample of water is a tedious and complex procedure, and most information necessary can be obtained from a partial analysis in which only those substances are determined that are present in larger proportions and that have undesirable effects in a boiler. Suspended matter is mainly hydrated silica, alumina, and ferric oxide. The two dissolved gases of significance are carbon dioxide and oxygen. Waters containing hydrogen sulfide are rather rare and not suited to use in steam boilers. An analysis of the dissolved material is best reported in terms of the ions actually determined. Entirely

wrong conclusions may be drawn from assuming presence of compounds. It should be realized that these materials are in such extremely dilute solution in water that ionization is practically complete; that only an elaborate phase rule study of each individual water would show how each component would separate under given conditions; and that all necessary information can best be secured by knowing what ions are present and the effect of each ion.

The ions ordinarily present in water in appreciable amounts are:

BASIC IONS

Calcium, Ca^{++}
Magnesium, Mg^{++}
Sodium, Na^+
Potassium, K^+

ACID IONS

Bicarbonate, HCO_3^-
Sulfate, SO_4^{--}
Chloride, Cl^-

It is always necessary to determine the amount of hydrogen ion, H^+ , present, but this is usually less than its concentration in pure water, and waters in the main are regarded as alkaline. Exceptions are mine waters, which contain free sulfuric acid from the oxidation of pyrite, and waters contaminated with acid industrial wastes. Ferric iron and aluminum are probably present as hydrous oxides. Silica is commonly thought of as being present as colloidal silicic acid but silicate ions may also be present. Chemically treated waters, and those which have been boiled or which have stood a long time in reservoirs, should be tested for carbonate ion. Nitrates are rarely present in appreciable amounts. Such ions as barium, lithium, manganese, phosphate, bromide, iodide, and borate may be present in small amounts, but they are usually neglected. Waters containing appreciable amounts of calcium and magnesium ions are called "hard" waters, and any process that removes these ions more or less completely is called "softening."

There are several units used in reporting water analyses, including "grains per gallon," "parts per million," and "milligram equivalents per liter." The terms "parts per million" may be used with any system of weights. The use of milligram equivalents has become increasingly popular among chemists and engineers. It has the advantage of greatly simplifying calculations and making comparisons and interpretations clearer and easier. In the treatment of water the unit used is "pounds per thousand gallons."

Even the smaller boiler plants regard clean water as an essential. What is to be considered here is the dissolved material in clean water. Evaporation is extremely rapid, and in time just as serious trouble can arise from small amounts of dissolved material as can develop in a

shorter time with greater concentrations. These troubles may be summed up in these three terms: corrosion, scaling, and foaming. They are prevented by supplying the boiler with as high a quality of water as can be obtained by chemical means, and what is still more important, by careful regulation at all times of chemical conditions within the boiler.

The maintenance of the proper conditions within a boiler demands continual technical and scientific control of the highest order. Water conditioning is far more than preventing these troubles. Under modern conditions of high pressures and high ratings, their avoidance means protection of millions of dollars' worth of equipment, the continuity of operation of the entire factory or plant, and the safety and lives of the operating force. A heavy responsibility, therefore, rests upon the chemist in the control of the water supply of the power plant.

In the case of corrosion in hot-water lines and boilers the main effect is actual solution of the iron and its alloys, either uniformly or in numerous depressions or "pits" distributed over the surface. There is still another form of corrosion, known as "caustic embrittlement," the result of which is weakening and failure of the metal around seams and rivet holes.

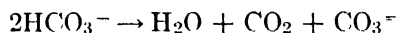
The ordinary form of corrosion appears to be solution of the metal in water. The higher the hydrogen ion concentration the more rapid is this solution. If the hydrogen ion concentration is that of pure water ($\text{pH}=7$) or is on the alkaline side and the water is free of dissolved oxygen, corrosion of this type is very slight. Most waters are naturally somewhat alkaline. In the prevention of scale a certain alkalinity is necessary. Hence it would appear that corrosion would be very simply avoided. However, all water that has been in contact with air contains dissolved oxygen. As the iron dissolves in the ferrous state it is oxidized by the oxygen in the water and appears as hydrous ferric oxide. The continuous removal of ferrous ions from solution favors further solution of the metal until the oxygen has been used up. Another explanation that has been rather generally offered for the effect of dissolved oxygen is that, as the iron dissolves, hydrogen ion becomes neutral hydrogen and is strongly adsorbed on the surface of the metal, the effect being essentially a polarization phenomenon. The dissolved oxygen is regarded as a depolarizer, permitting the solution of the metal to proceed without hindrance.

The excessive corrosion in pits is explained by the formation of gaseous bubbles, as air and other gases are driven out of the water by heat. The oxygen of the bubble is soon exhausted, and with respect

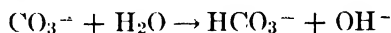
to oxygen the bubble functions as a vacuum. More oxygen is supplied to the interior of the bubble from the surrounding solution. The continual feeding of oxygen to the bubble means continual corrosion of the metal and formation of a pit.

Hence prevention of corrosion due to actual solution of the metal is prevented by making the water slightly alkaline, and by removal of dissolved oxygen. Corrosion of this type is more common in hot-water lines. The removal of dissolved oxygen is most easily accomplished in open feed-water heaters. Steam passes through the water and sweeps out the gases. Excess steam is condensed beyond the heater, and the gases pass on. Dissolved oxygen is also removed by heating the water under reduced pressure, but heaters operating at atmospheric up to 30 lb. pressure are more common. In the more primitive boiler plants, corrosion is often prevented by a thin coating of scale, but it is practically impossible to regulate scale thickness, and this method of protection is uncertain and inefficient.

The second type of corrosion is generally referred to as caustic embrittlement. It manifests itself by the development of fine cracks along seams and rivet holes and a very great weakening and embrittlement of the metal. The cracks are definitely intercrystalline, the attack being apparently on the material between the metal grains. This embrittled condition is known to be present in the steel of caustic soda evaporators. It also often characterizes boiler metal continually exposed to waters high in bicarbonate ion and low in calcium ion. It is well known that bicarbonate ion decomposes under the influence of heat.



The resulting carbonate ion at high temperatures and pressures very rapidly hydrolyzes.



The bicarbonate enters the cycle again, and the net result is increase of alkalinity. It appears extremely probable that the main chemical cause of caustic embrittlement is the action of the iron on the concentrated sodium hydroxide solutions segregated in seams and around rivet holes. Hydrogen is evolved and functions as an embrittling agent. The cementing material between the fine crystals making up the alloy dissolves, cracks develop, and the whole structure of the metal is seriously damaged.

Caustic embrittlement is often confused with another phenomenon known as "corrosion fatigue." When metal exposed to water is sub-

jected to constantly recurring intermittent or cyclic stresses, even though they are far below the endurance limit of the metal, cracks appear that are often transcrystalline, although intercrystalline cracks are known. This effect is not confined to seams and rivet holes, but occurs anywhere in the boiler, and even when the water is neutral or only slightly alkaline. Periodic or cyclic strains certainly accelerate caustic embrittlement by permitting penetration of water into cracks already starting, but the effect here is primarily a matter of excessive alkalinity.

Since caustic embrittlement depends on alkalinity it may be partially prevented by keeping the alkalinity of the boiler water at a reasonably low figure. At the same time, the water must not get over into the acid range because of danger of the solution type of corrosion, and scale cannot be prevented unless some alkalinity is maintained. Furthermore, it is not safe to depend on mild alkalinity throughout the boiler preventing the development of a highly alkaline condition in the seams. The answer to these contradictory requirements is the presence of sulfates in the water. Whatever the explanation of their effect, it is certain that sulfates prevent caustic embrittlement. The amount necessary for safety depends on the pressure used. The American Society of Mechanical Engineers in its boiler code recommends definite ratios of sulfate (as sodium sulfate) to alkalinity (as sodium carbonate). The ratio varies from 1 : 1 for low pressures (up to 150 lb.) to 3 : 1 for high-pressure boilers.

Scale forms primarily by crystallization of substances at the point of least solubility. Most substances are more soluble in hot water than in cold water. Unfortunately, calcium sulfate is much more soluble in cold water than in hot. Both calcium and sulfate ions are commonly found in water supplies. Certain silicates, particularly magnesium silicate, also have this same sort of solubility curve. The hottest place within a steam boiler is obviously where hot gases and radiant heat from the fuel bed come in contact with the boiler flues or tubes. Those substances less soluble at higher temperatures and more soluble at lower will naturally begin to crystallize at the hottest part of the boiler, and will form a scale of adhering and interlacing crystals. Part of the precipitate is due to evaporation from the edges of bubbles and part to crystal growth from supersaturated solutions. The bicarbonate ion is decomposed in hot water. The resulting carbonate ion combines with calcium ion. Since the solubility product of calcium carbonate is very low, precipitation takes place at once. Calcium carbonate decreases in solubility only very slightly with

increasing temperature, and does not form scale so readily at the heating surfaces. It is capable of only very little supersaturation, and crystals that form on the metal readily break off in flakes to form a sludge. Considerable quantities of calcium carbonate sludge will be mechanically caught in the tangled mass of calcium sulfate crystals, but in the absence of sulfates no appreciable amount of scale will form. The main cause of scale in the boiler is the formation of calcium sulfate, supplemented by magnesium silicate. Hot-water line scales are primarily calcium carbonate because of decomposition of bicarbonate ion, the relief of supersaturation at the solid-liquid interface, and delayed reactions of softeners.

In comparison with the magnitude of film resistance, the resistance of scale to the passage of heat is small. In locomotive boilers and in the older type of stationary boilers that have little or no provisions for heat exchange, heat losses are high. In low-pressure boilers, scale thicknesses were attained that are unthinkable in modern practice. Modern boilers equipped with a large number of tubes and with adequate surfaces for heat exchange suffer relatively little actual heat losses from scale. If scale develops in one part of the boiler, and heat transfer is hindered, the load is merely shifted to another part of the boiler where there is water that has not reached the stage of scale formation. The effect of low thermal conductivity is much more serious than loss of heat. The heat applied from the fire side of a tube is not quickly transferred to the water, with the result that the metal reaches such a temperature that its tensile strength is materially lowered. The insulating effect of scale varies to some extent with its composition but to a much greater extent with its porosity and the amount of gas space it contains. Almost unbelievably thin but very porous silicate scales will so hinder heat transfer as to be sources of very great danger. This effect becomes increasingly serious with high pressures. Since pressures of 400 to 600 lb. are becoming quite common, and there are several industrial plants and a still larger number of power plants operating at pressures of 1200 to 1800 lb., the matter of absolute scale prevention becomes of extreme importance. A few boilers in the world are now operating at the critical pressure of steam, indicating the general trend of power development.

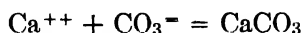
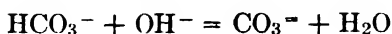
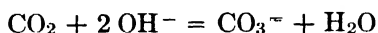
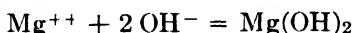
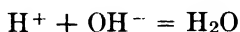
Scale may be prevented in the first place by removing, as far as possible, calcium and magnesium ions from the feed water, and secondly by so regulating the concentration of ions within the boiler that the solubility product of any scale-forming compound is not reached. Unfortunately, attention has been too greatly centered on the compo-

sition of the boiler feed water, and not enough consideration has been given to conditions within the boiler itself.

"Boiler compounds" are substances intended to prevent boiler troubles. Many of these are either useless or actually harmful. There is a very definite objection to the use of material whose composition is not known to the user, and whose effects are not clearly understood. Some substances may be added to raw boiler feed water with advantage, the most important being sodium carbonate and sodium phosphate. A water containing any considerable amount of scaling material should be subjected to chemical treatment outside the boiler, followed by the use of sodium carbonate or sodium phosphate in the boiler in order to maintain optimum conditions. This is known as internal conditioning. If the amount of scaling ingredients is not large, it is quite possible to add to the feed water those substances required to prevent scaling.

The two important things to be remembered are that the boiler should have fed to it a water that is as low as possible in calcium and magnesium salts, and that conditions which make scale formation impossible should be maintained continually within the boiler. The problem is confined largely to materials brought in by make-up water added to compensate for steam losses. The composition of the water, the design of the boilers, the pressure maintained, the preheating facilities for bringing feed water up to the boiler temperature before introducing it into the boiler, the amount of condensate and make-up must all be taken into consideration.

The two most important methods of softening water outside the boiler are the lime-soda and the zeolite processes. The lime-soda process involves adding to the water the correct amount of a suspension of calcium hydroxide and sodium carbonate, these two substances being the cheapest source of the hydroxyl (OH^-) and carbonate (CO_3^{--}) ions, and subsequent filtering to remove precipitates. The following equations represent the removal of undesirable ions and the formation of insoluble substances, which are gotten out of the water by settling and filtration:



Calcium ion is thus added to the water in equivalent amount to hydroxyl. The carbonate ion, produced both from dissolved carbon dioxide and bicarbonate ion, removes its equivalent weight of calcium. The remaining calcium ion is taken out with the carbonate ion derived from the soda ash. An analysis of the water, giving the amount of calcium, magnesium, hydrogen, and bicarbonate ions, and also free carbon dioxide, is sufficient to determine the amount of lime and soda necessary. Owing to incomplete reactions and occlusion of reagents in precipitates, it is usual to use somewhat larger amounts than theoretically required.

The control of lime-soda softeners is relatively simple, although an understanding of the chemistry involved requires training in quantitative analysis and fundamental physical chemistry. When outside treatment is followed by internal conditioning, the difficulties of exact control of a softener vanish. The control in this case is a matter of alkalinity.

Lime-soda softeners are of two general types, intermittent and continuous. The intermittent softener operates at the temperature of the water from well or reservoir; a continuous softener may be run either cold or hot. An intermittent softener is essentially a large tank or reservoir equipped with feed tanks for chemicals, a floating drain pipe to decant the treated water from the precipitates, and a sludge valve to allow cleaning of the tanks. Such softeners have all the disadvantages of batch operations, and are not extensively used. A continuous cold process softener is usually made up of a tank within which is a cylinder open at the top and bottom. The chemicals and the raw water are mixed by proportioning devices, and the mixture passes down inside the cylinder, where it is vigorously stirred. The speed of flow is adjusted to permit reactions to go most of the way towards completion. The water, carrying a suspended sludge, rises in the annular space between the cylinder and the walls of the tank, and in this quiet zone settling takes place, most of the precipitate falling to the conical bottom of the softener, whence it is discharged. The water still carries some solids in suspension, and these are removed by a filter. The removal of calcium and magnesium is by no means complete in cold process softeners, and such water is apt to produce some sludge and scale in boilers. Sodium aluminate is now quite generally used along with lime and soda ash in both hot and cold softening plants for improvement of coagulation and settling and for the removal of the larger part of the calcium and magnesium not ordinarily precipitated by the lime and soda ash.

A combination feed water heater and softener is often employed. It is usually an insulated cylindrical tank with a conical bottom, and

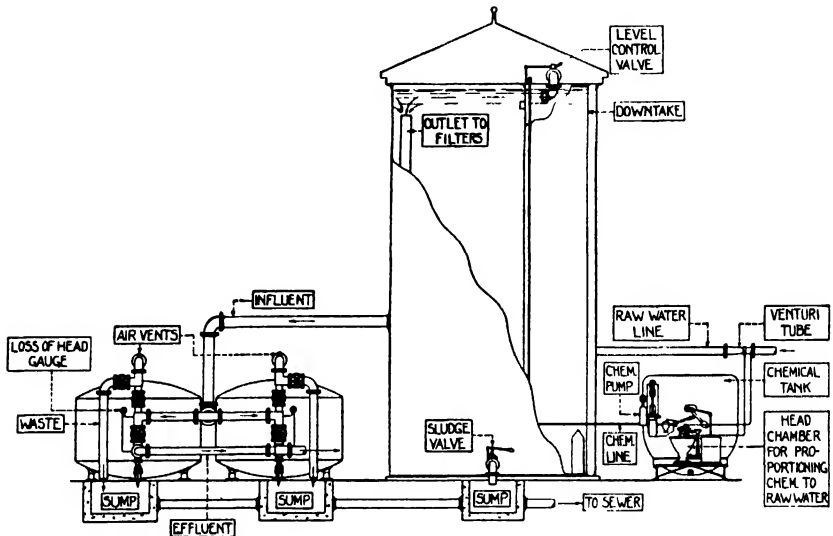


FIG. 55.—Cold Process Lime-Soda Softener. Elevation. Courtesy International Filter Company, Chicago, Ill.

above it is a superimposed mixing chamber equipped with baffles into which the raw water and chemicals are fed while exhaust steam is admitted. The temperature attained is practically that of boiling

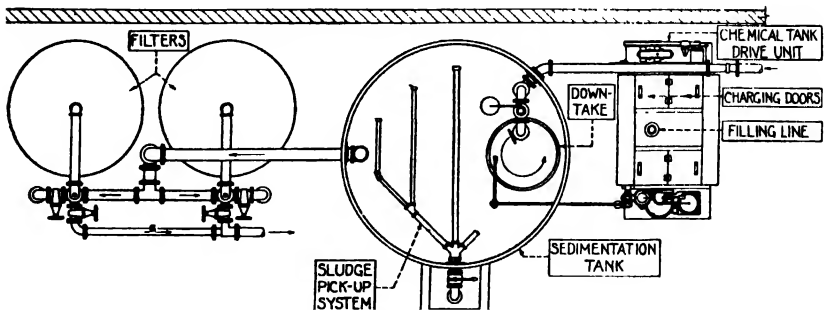
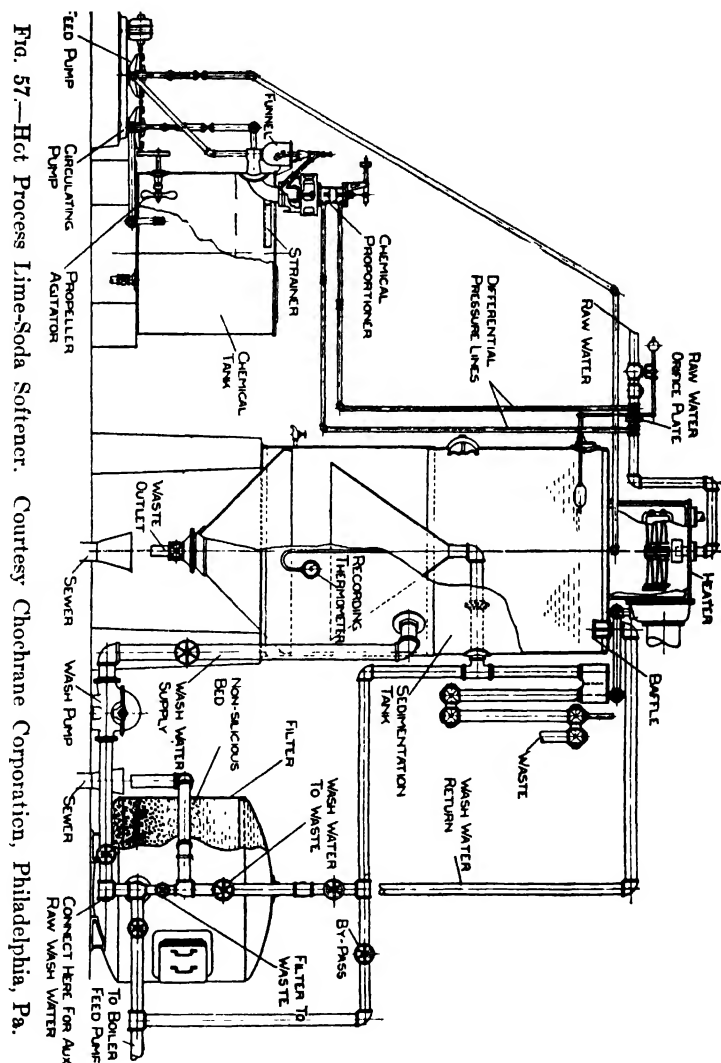


FIG. 56.—Cold Process Lime-Soda Softener. Plan. Courtesy International Filter Company, Chicago, Ill.

water, and the reactions are quite rapid and go practically to completion. The solids settle rapidly to the bottom, while relatively clear

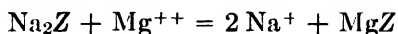
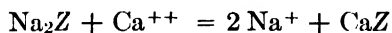
water is drawn off from under a protecting cone, and after filtration passes directly to the boiler.

Zeolites are complex silicates of aluminum and alkali metals.



Those most generally used for softening water are artificially prepared, but some natural zeolites may be used. An alkali aluminum silicate in contact with solutions containing calcium and magnesium ions will undergo a transformation, the alkali metal being liberated as

an ion, and the calcium or magnesium ion taking its place in the insoluble compound. This is probably a selective adsorption, followed by chemical reaction. Assuming a typical zeolite to have the formula $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot 6 \text{H}_2\text{O}$, and calling all the compound except sodium Z, the following reaction takes place:



The reactions are readily reversible. Contact of spent zeolite with a strong solution of sodium chloride results in the restoration of the substance to its original composition with the freeing of calcium and magnesium ions. The brine carrying these ions is drawn off, and after being washed, the zeolite bed is ready to function again as a softening agent. The material can be regenerated in fifteen minutes by contact with a 10% sodium chloride solution. The zeolite occupies a considerable portion of the tank, being supported by gravel on a perforated plate. A layer of crushed marble held on a grid above the zeolite serves to remove dissolved carbon dioxide. The softener is equipped with brine tanks and suitable connections and valves for feeding, regenerating, washing, and draining. It resembles very closely an ordinary sand and gravel pressure filter. Clean, raw water must be used. During the early part of the run, calcium is often as low as 0.5 p.p.m.; by the middle of the run it is of the order of 1 to 2 p.p.m., and in the latter part, more than 2 p.p.m. No acid ions are removed, and sodium ion is added to the water in amounts equivalent to the calcium and magnesium ions. If a large amount of bicarbonate ion is objectionable, the zeolite-treated water may have added to it a sufficient amount of sulfuric acid to bring the hydrogen ion concentration up to that of pure water. In small installations it is extremely difficult to mix the small amount of acid with the large amount of water. Large installations can afford adequate equipment. Acid treatment is followed by removal of the carbon dioxide generated, and the pH of the water is continuously and automatically recorded and controlled.

Foaming in a steam boiler is the accumulation of stable bubbles of gas that are coated with liquid films of such thickness that water is mechanically carried over into the steam lines. Water in the steam causes hammering effects in engines and is likely to throw turbines badly out of balance. This is entirely a phenomenon of solutions, since pure liquids do not foam. Assuming a properly designed boiler, foaming appears to depend on the concentration and composition of

the dissolved substances in the boiler water. The methods of chemical treatment of water to prevent scale lead to an increase in the total dissolved solids. The removal of calcium ion also makes a water more susceptible to foaming.

The essential features of the theory of foaming advanced by Professor C. W. Foulk are that there are differences in concentration of dissolved material in the surface of a liquid at the gas-liquid interface and in the main body of the liquid, in some cases the film having higher and in other cases lower concentrations; and that when two bubbles approach each other and try to coalesce, or when a bubble tries to break through the surface of liquid, considerable work must be done and coalescence does not take place. In the case of a pure liquid, there are no concentration differences, and the bubbles coalesce or break the surface readily.

Sodium carbonate has been regarded as particularly pernicious in causing foaming, but its effect appears to be that it removes calcium. It is a well-known fact that solutions containing calcium salts along with small amounts of tannates do not foam, but that removal of calcium causes vigorous foaming. Suspended matter has also been charged with causing foaming, the explanation being that the suspended matter enters into the film surrounding the bubbles and gives them mechanical strength. However, experience has shown that a boiler may contain suspended matter without foaming. The character of the suspended matter is important, that material which has adsorbed oil being particularly objectionable.

A number of organic compounds, some of them in surprisingly small amounts, will inhibit foaming. Since such substances are susceptible to hydrolysis and decomposition with the formation of undesirable and even dangerous compounds, their use is not regarded as safe. An exception is in locomotive boilers, in which violent agitation and vibration make foaming particularly great, and whose contents are changed after a few hours of service.

The main remedy for foaming lies in an intelligent regulation of the amount of dissolved solids in the water of the boiler. The alkalinity should be kept down to the minimum necessary to give protection against corrosion, and the concentration of salts should be lowered at intervals by removing a part of the boiler water and replacing with feed water. There are conditions under which some foaming is inevitable, if other troubles are to be prevented, but very efficient mechanical separators are in use that will prevent water passing from the boiler with the steam.

It is important to supply a boiler with as high-grade water as possible. It is still more important to maintain such conditions within the boiler that foaming, corrosion, scale, and embrittlement will be reduced to a minimum. Sometimes the nature of the feed water is such that it is impossible to prevent all these troubles occurring. In this case, it is best to choose the least of all the evils and one whose effects can be mechanically counteracted, namely foaming. Regardless of the initial concentrations of ions in the water, continued evaporation will increase the concentration to a point where troubles are bound to occur. Satisfactory control of initial boiler conditions may be secured by determining the carbonate, hydroxyl, and sulfate content of the boiler water. With pressures over 250 lb. per square inch, it is difficult to maintain sufficient excess of carbonate ion to prevent formation of calcium sulfate scale, although recent work indicates the possibility of using carbonate conditioning at higher pressures than previously considered possible. Sodium phosphate has been extensively used in high-pressure boilers. Ordinary disodium phosphate has the disadvantage of causing scale in feed water lines. This has led to the substitution of sodium metaphosphate, NaPO_3 , which is not appreciably changed to monosodium phosphate, NaH_2PO_4 , until subjected to boiler temperature and pressure. Because of its buffer action it serves to regulate hydrogen ion concentration. Sodium aluminate is also widely applied, either alone or with other softening agents, directly to the boiler as an internal softening and coagulating agent.

The question involved in boiler water conditioning is the relation of the concentration of carbonate or phosphate to the concentration of sulfate ions. Given the following equations at the same temperature,

$$[\text{Ca}^{++}][\text{CO}_3^{--}] = K_1 \quad \text{and} \quad [\text{Ca}^{++}][\text{SO}_4^{--}] = K_2,$$

it is obvious that calcium ion is common to both equations and can be eliminated to give

$$\frac{[\text{CO}_3^{--}]}{[\text{SO}_4^{--}]} = \frac{K_1}{K_2}$$

The same sort of result has been worked out for phosphate and sulfate concentrations. By including such factors as activity coefficients and ionic strengths in the calculations, it has been found that carbonates are effective in smaller concentrations and at higher temperatures than were at first indicated. For example, a boiler operating at 150 lb. pressure will require carbonate ion only to the amount of 1% of the concentration of sulfate ion, whereas earlier calculations called for 9%.

FUELS

Fuels may be classified according to the state in which they are used, gaseous, liquid, or solid.

The main combustible components of all industrial gases are given in the following table:

Name	Formula	Combustion Reaction	HEATING VALUE *	
			Gross	Net
Hydrogen	H ₂	2 H ₂ + O ₂ = 2 H ₂ O	324	273
Carbon Monoxide . .	CO	2 CO + O ₂ = 2 CO ₂	321	321
Methane	CH ₄	CH ₄ + 2 O ₂ = CO ₂ + 2 H ₂ O	1012	912
Ethane	C ₂ H ₆	2 C ₂ H ₆ + 7 O ₂ = 4 CO ₂ + 6 H ₂ O	1755	1605
Benzene	C ₆ H ₆	2 C ₆ H ₆ + 15 O ₂ = 12 CO ₂ + 6 H ₂ O	3956	3797
Ethylene	C ₂ H ₄	C ₂ H ₄ + 3 O ₂ = 2 CO ₂ + 2 H ₂ O	1598	1492
Propylene †	C ₃ H ₆	2 C ₃ H ₆ + 9 O ₂ = 6 CO ₂ + 6 H ₂ O	2387	2233
Acetylene	C ₂ H ₂	2 C ₂ H ₂ + 5 O ₂ = 4 CO ₂ + 2 H ₂ O	1490	1440

* The heating value is given with the gases measured at 60° F and 29.92 in. of mercury. The gross value represents the total heat obtainable if the steam produced by combustion is condensed; the net value assumes that there is no condensation of steam. The values are in terms of B.t.u. per cubic foot.

† Propylene is taken as typical of higher unsaturated hydrocarbons.

Other compounds are present in small amounts, but those given above are the ones most commonly present. In addition, there are varying amounts of non-combustible gases, including nitrogen, N₂ (with which is included argon and in some natural gas also helium), oxygen, O₂ (which lowers the heat value of the gas but also lowers the amount of air required for combustion), and carbon dioxide, CO₂. Water vapor is not taken into consideration, since most gases are measured and handled over water. Although analyses of gases are made with the gas saturated with water vapor, the results of the analysis are reported on a dry basis, giving the relative amounts of other components.

The heating value of a gas is determined by means of calorimeters of various types. The rise in temperature of given amounts of air, or more commonly water, caused by burning measured quantities of the gas, is the principle underlying gas calorimetry.

Natural gas is a combustible gas found often under great pressure in pockets under the surface of the earth. Although practically all

petroleum is associated with gas under pressure, most natural gas is obtained from wells from which no petroleum is being taken. Burrell and Oberfell give the methane content of natural gas as varying from 50% up to 98%, and ethane from none up to 31%. The heat value varies from 700 to 1150 B.t.u. per cubic foot gross. Natural gas from Texas' fields has been for several years the source of helium, the amounts of this valuable gas being of the order of 1% to 1.75% of the total volume of the gas. Helium is removed by liquefying the other components of the gas by refrigeration and compression. Natural gas is now piped over the larger part of the United States.

Coal is carbonized at temperatures of the order of 1600° F. to 2000° F. with the production of a gas which has an average heating value of 600 B.t.u. The residue left in the carbonizing apparatus is known as coke. Tar, ammonia, and various minor substances are removed from the gas. The term "coal gas" is often applied to the product of retorts, and "coke-oven gas" to the product of coke ovens, but the gas in each case is practically the same, being made up largely of methane and hydrogen.

What is known as "water gas" is the product of the action of steam on highly heated carbon. The term "blue gas" is often given to this product, since it burns with a blue, non-luminous flame. It is composed mainly of hydrogen and carbon monoxide, and is used comparatively little alone, but is enriched with oil gas made by cracking petroleum distillates or residues. The same equipment in which cracking takes place is heated by the waste gases from blue gas manufacture. This product, known as "carburetted water gas," is very widely distributed by public service companies as an industrial and domestic fuel. It has a heating value averaging about 550 B.t.u.

What is known as "producer gas" is made by the continual passage of air and steam through a deep bed of fuel. Its main combustible component is carbon monoxide, since this substance results from the reduction of carbon dioxide as well as steam. Hydrogen is present in proportion to the amount of steam used to cool the grates and to prevent clinkers. Obviously the main component is nitrogen from the air. If bituminous coal is used as a fuel, the gas will contain some methane and illuminants formed by carbonization of the coal. Producer gas has a heating value of 120 to 180 B.t.u. Because its low heating value makes storage and transportation unprofitable, producer gas is manufactured almost entirely by its users.

Other industrial fuels include blast-furnace gas, used principally by steel mills; oil gas, made largely by cracking petroleum residues in the

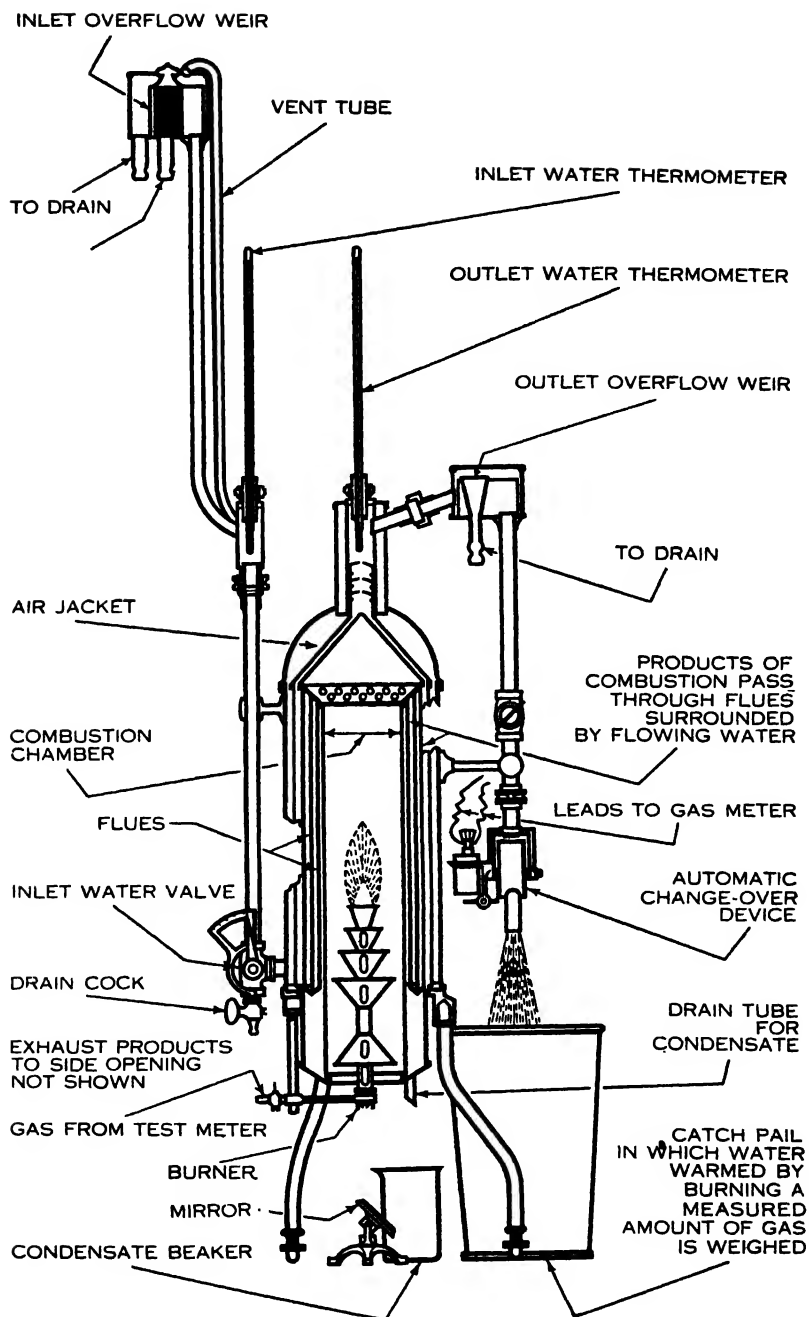


Fig. 58.—Continuous Gas Calorimeter (Sargent Automatic). Courtesy Precision Scientific Company, Chicago, Ill.

presence of air or more commonly steam; butane gas, separated as a liquid from natural gas and marketed in cylinders in that form; propane gas, separated either from natural gas or from oil-refinery gases; acetylene, made by the action of water on calcium carbide; and refinery gases, which are by-products in the distillation and cracking of petroleum.

Liquid fuels are largely petroleum products. Motor fuel is composed of the more volatile liquids directly distilled from crude petroleum or made by thermal decomposition of higher petroleum distillates. Such products are commonly known as gasoline. Oil engines of the Diesel type use less volatile distillates and even some crude petroleums. Very large quantities of petroleum distillates are used for house-heating purposes. There is still considerable use of distillates of the grade of lamp oils or kerosene in cook stoves and small portable stoves. Comparatively little crude petroleum is used directly as fuel. Partial distillation to recover gasoline and light fuel is known as "topping," and the residue is referred to as "topped crude." Such materials are used in very large quantities by railroads, steamships, and power plants. Heavy residues from petroleum refining are often burned under the stills in which they were produced. The residues from the thermal decomposition, or cracking, of gas oil for the production of gasoline constitute probably the largest source of fuel oil. Distillates, cracked residues, and even topped crudes are used in the carburetted water gas process. Considerable quantities of coal tar are burned by steel mills operating coke-oven plants.

The chief things to be determined in evaluating a liquid fuel are: its viscosity at different temperatures as a measure of the ease with which it may be pumped; the specific gravity, which gives the weight of a unit volume; and the heating value in B.t.u. per pound and per gallon. The heating value is primarily a function of specific gravity, since the components of most petroleums of the same specific gravity are sufficiently alike to permit the use of a formula that gives values agreeing with calorimetric determinations to within 1%. B.t.u. per pound = $18,650 + 40 (\text{degrees Baumé} - 10)$.

The chief solid fuels are coal in all its varieties, and coke, which is a coal product. Wood has practically ceased to have any significance as a power plant fuel, although wood wastes are burned at sawmills and wood pulp plants.

Gaseous and liquid fuels are practically homogeneous, and thus present no difficulties in sampling. Coal, however, is made up of true coal substance, which itself is not entirely homogeneous, and extrane-

ous mineral matter of the nature of rock, shale, and slate. It occurs in layers in veins of varying thickness, and even with the utmost care in mining carries with it some non-coal materials. In order that the accuracy may be within limits of analytical error, there must be a definite ratio between weight of the total sample and the weight of the largest single particle, which may be regarded for purposes of calculation as composed solely of non-coal substance. This ratio is of the order of 10,000 : 1. If the coal is composed of large lumps or is "run of mine," it is extremely difficult to secure a representative sample. Smaller sizes are easier to sample, and powdered coal presents very little more difficulty in sampling than a liquid.

Analyses of coal are of two kinds, ultimate and proximate. An ultimate analysis of coal includes carbon, hydrogen, oxygen, nitrogen, sulfur, and ash, and it is carried out only in connection with scientific investigations of coal composition. Carbon determinations, however, are easily made by fusing the coal with sodium peroxide and measuring the carbon dioxide evolved by the action of acids on a solution of the products of fusion. A proximate analysis is the one most commonly made. Even though its terms are purely relative, arbitrary, and empirical, it is capable of giving sufficient information concerning a coal to determine its usefulness for a given purpose. The following values are determined in a proximate coal analysis.

Moisture. Loss in weight caused by heating a sample one hour in a current of dry air at 104° C. to 107° C.

Ash. Non-combustible residue produced by heating a sample at 750° C. in a muffle furnace with ample access of air until constant weight is attained.

Volatile Matter. The difference between total loss of weight and moisture value of an undried sample when heated for 7 minutes in a platinum or heat-resisting alloy crucible of special shape and fitted with a special cover in a furnace held at 950° C.

Fixed Carbon. The difference between the sum of the moisture, ash, and volatile matter and 100%.

Sulfur. The general principle of all sulfur determinations is the oxidation of all sulfur and sulfur compounds of lower valence to the sulfate condition and determination of the total sulfate. This is accomplished by heating a sample until all combustible material has been burned out in the presence of sodium carbonate and magnesium oxide; by fusing the sample with sodium peroxide; and by burning the sample in oxygen under pressure in a calorimeter bomb.

Heating Value. The heating value of both liquid and solid fuels

may be determined with a fair degree of precision by mixing a sample with sodium peroxide, placing the mixture in a closed vessel, igniting with an electrically heated wire, and determining the rise in temperature of a weighed quantity of water. Allowance has to be made for heat developed by a number of reactions other than simple oxidation. A more precise method involves burning the fuel in a calorimeter bomb containing oxygen under heavy pressure. By the use of vacuum jackets surrounding the vessel containing the water and the oxygen bomb, cooling corrections are unnecessary, and only relatively small

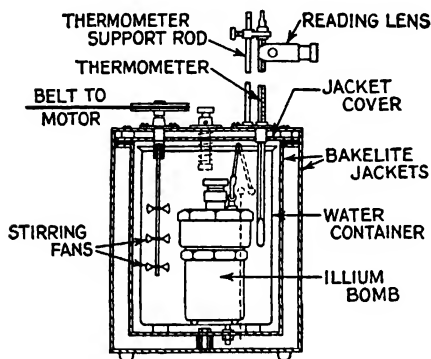


FIG. 59.—Parr Oxygen Bomb Calorimeter
Courtesy Burgess-Parr Company,
Chicago, Ill.

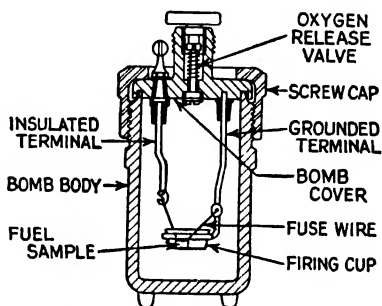


FIG. 60.—Cross Section of Parr Oxygen Bomb. Courtesy Burgess-Parr Company, Chicago, Ill.

corrections for the formation of nitric and sulfuric acids and the heat of the fuse wire need to be made.

Fusion Point of Ash. It is very essential to know at what point the mineral residue from the burning of coal will fuse. This is determined by making a cone of the ash, using dextrin as a binder, and heating it until it bends over, the temperature at which the top of the cone touches its supporting base being recorded as the ash fusion point.

A value developed by the late Professor Parr of the University of Illinois and known as "unit coal" has considerable value in the classification of coal. This refers to the amount of combustible material in the coal, with proper allowance for the various forms of sulfur. The heating value of the "unit coal" in a sample is arrived at by the following formula.

$$\text{B.t.u. of Unit Coal} = \frac{\text{B.t.u. as determined (dry basis)} - 5000 \times \text{Sulfur}}{1 - (1.08 \times \text{Ash} + 0.55 \times \text{Sulfur})}$$

Obviously the sulfur and ash values are given in decimal fractions

and not percentages. It is reasonable to suppose, and the assumption is generally correct, that coal from a given vein is made of the same kind of organic matter, and differs only in moisture and non-combustible substances. If allowance is made for moisture, ash, and sulfur, the heating value of the combustible material should be practically constant. Once this is determined, it is possible to substitute this value in the above formula, and from the moisture, ash, and sulfur values to arrive at the heating value of any sample from this mine or formation.

Leaving out all questions of origin, and also those of detailed physical structure, coal may be generally divided into these classes, the method of classification being the one devised by Parr.

FUEL	B.T.U. OF UNIT COAL
Cellulose and Wood	6,500- 7,800
Peat	7,800-11,500
Brown Lignite	11,500-13,000
Black Lignite (sub-bituminous)	13,000-14,000
Bituminous (Mid-continent)	14,000-15,000
Bituminous (Eastern)	15,000-16,000
Semibituminous and Semianthracite	15,500-16,000
Anthracite	15,000-15,500

A more thorough understanding of the mechanism of combustion has led to great improvements in the design of furnaces and fireboxes under steam boilers. The fuel is most generally spread in a relatively thin layer on grates, and air is admitted from beneath the grates. The air rises only a very short distance before all the oxygen has combined with carbon to form carbon dioxide. This reaction produces intense heat. As the carbon dioxide rises, it reacts with highly heated carbon to form carbon monoxide. As this escapes from the top of the fuel bed, it meets an additional supply of air and burns in a long flame. If all the combustible material of coal were carbon, the problem would be much simplified. Coal is made up of a number of complex organic compounds, mixed with inorganic substances in varied proportion. Under the conditions of destructive distillation obtaining when fresh coal is fed on a bed of red-hot coke, the products combine with oxygen to form excessive quantities of soot, which appears as black smoke. This not only constitutes a nuisance, but also represents a waste of valuable combustibles. If the fresh coal is allowed to heat slowly in the presence of an excess of air, oxidation compounds will be formed, the oxygen being in hydroxyl and carbonyl groups. These products subsequently decompose with the evolution of heat, but without for-

mation of free carbon. Modern furnaces equipped with mechanical stokers are designed on the basis of the fundamental principles of combustion, with the result that little or no black smoke is given off.

It has been shown earlier in the text that fine powders can be handled in very much the same way as liquids. There are certain definite advantages, particularly in large installations, in burning coal in finely divided condition. In order to get satisfactory grinding, a current of warm, dry air may be passed through the pulverizing equipment. The fine coal that passes the separators is blown into the furnace and burned very much as a jet of oil droplets or a true gas. Burners have been developed that can be adjusted to coals of widely varying volatile matter. The correct amount of air is automatically admitted with the powdered coal through a nozzle into the firebox, and a long brush of flame results. Combustion is practically complete, and the resulting ash is removed from the stack gases by baffles, settling chambers, electrostatic separators, and air filters. If the coal has an ash with a low fusion point, it may be burned in such a way that the ash fuses and is drawn off as a slag from the bottom of the furnace.

LUBRICANTS

Metal surfaces are not perfectly smooth even though they appear to the eye to be so, but are made up of microscopic hills and hollows. When such surfaces are rubbed upon each other, the motion is impeded by collisions between the higher areas, and heat and wear of surfaces will occur. The greater the pressure the greater will be the difficulties of moving the surfaces over each other. In some cases, enough heat is developed to cause incipient fusion of the metal surfaces so that they actually weld together.

In order to operate machines successfully it is necessary to introduce substances between the metal surfaces that will prevent heat and wear. These substances are known as lubricants. They must offer comparatively little internal resistances so that the layers that adhere to the metal surfaces slip over each other easily and with relatively little loss of power.

Many liquids and a few solids possess lubricating properties to a remarkable extent, but comparatively few have industrial importance. Lubricants may be divided, according to their physical state, into true liquids, plastic solids, and true solids. A true liquid will flow, theoretically at least, upon the application of the slightest pressure; a plastic solid will not change its shape until a certain pressure known

as "yield value" has been reached. Each type serves a definite purpose in industry. The most generally used lubricants, however, are in the liquid class, and for the most part possess those physical properties associated with the term "oil."

Although lubricants made from vegetable and animal oils exclusively have been very generally displaced by petroleum products, there is still a very definite place in the lubricant field for such materials. Castor oil, lard oil, and tallow oils are most widely used. Their chief value lies in the ability to support heavy loads and to adhere to metal surfaces in the presence of water. In most cases, however, glycerides are blended with petroleum oils. There are certain conditions where a mixture of fatty oils with petroleum oils is better than either type alone. Glycerides are blended with petroleum oils, principally for the lubrication of steam cylinders under saturated steam conditions, a more permanent and tenacious film being secured. Both lard and tallow oils are used in amounts up to 10%. Fatty acids such as oleic acid have a limited use in small amounts in a few automobile lubricants. The chief objection to glycerides and fatty acids is their tendency to decompose, oxidize, and form gummy deposits. Lubricants containing fatty oils or fatty acids are practically restricted to that type of equipment in which they are used only once. They emulsify so readily with water that their recovery is difficult. Fatty acids in amounts more than 2 or 3% are apt to cause corrosion. Fatty oils are also more expensive than mineral oils.

Lubricating oils are made from petroleum by processes of distillation, which are discussed in the chapter on petroleum. In a very general way, it may be said that they are primarily hydrocarbons of high boiling point. Since they are fairly easily decomposed by prolonged heating at their boiling points, special methods of obtaining these products are necessary, including the use of pipe stills, low pressures, and steam. Fractionating bubble plate columns are employed in order to insure thorough separation from lower-boiling components. Steam cylinder oils are residues from high-grade paraffin base crudes, from which the lighter and more volatile materials have been removed by the use of steam and vacuum.

Lubricants are further refined by means of treatment with sulfuric acid and with adsorbing clay. Some lubricating oils may be treated with clay alone, but for most purposes more drastic refining is necessary.

As a class, steam turbine oils require the most careful treatment because of severe conditions of service. When properly made, mineral

lubricating oils are exceptionally stable, and in well-designed machinery will give very efficient service. For turbines, internal-combustion engines, and many other types of machinery, mineral oils are unequalled.

Straight oils such as lard oil have extensive use in lubricating the edges and points of tools that cut and shape metal, but emulsions of oil and water are also very generally employed where conditions are not particularly severe. These emulsions combine the lubricating power of oil with the high specific heat of water as a cooling agent. They are made by agitating the oil and water with such emulsifying agents as soap, sodium phenolate, sulfonated castor oil, and sulfonated mineral oils.

Grease as a lubricant is defined as a mixture of a mineral oil and a soap. Some greases may contain small quantities of fatty oils in addition to soap. Greases belong to the plastic solid class, and their value lies in their ability to resist small forces and to remain in place under conditions where liquids would flow away and be lost. They have real value in many places. Both calcium and sodium soaps are used as emulsifying agents. Some greases contain both types of soaps, but "cup grease" is commonly made with calcium soap, and "fiber" or "sponge grease" contains sodium soap. The difference between the action of the two soaps is that sodium soaps produce an emulsion of oil in water and calcium soaps an emulsion of water in oil. Aluminum and lead soaps are also used in grease making, and some greases contain mica and graphite. Tallow and petroleum jelly may also be used alone as greases.

Graphite is the most widely used of all solid lubricants. It may also be incorporated in metal, and, where service is intermittent, no other lubricant is necessary. Graphite is supposed to fill the hollows in metal surfaces, and being itself soft and slippery is thus expected to reduce wear and friction. It is true that graphite has real value, but it must be used with caution and under conditions where no complications can arise. It tends to lodge in ball races and feed lines and may eventually interfere with oil circulation, thereby defeating instead of improving lubrication. Lead has found use as an emulsion in copper for certain types of bearing. Lead will not alloy with copper, but finely divided globules of free lead remain, which aid materially in lubrication.

The mechanism of lubrication is neither simple nor well understood, hence it is necessary to rely on certain empirical and indirect measurements to grade lubricants. Friction measurements with stand-

ard bearings and under conditions duplicating those of service can be made, and they give some information. Few of the tests applied to lubricants are chemical, and most of them have to do with certain physical properties and characteristics. The choice of a lubricant depends primarily upon its behavior in use. Those which prove most valuable in actual operation are taken as standards, their properties determined, and specifications are written on this basis.

"Oiliness" is a property of lubricants that has come to be recognized in a qualitative way, but is not measurable. R. E. Wilson has defined oiliness as "that property by virtue of which one fluid gives a lower coefficient of friction than another of the same viscosity." It is probably due to a selective adsorption of certain compounds in the oil by the metal surface. The actual film that separates metal surfaces functions as a plastic solid of colloidal but not molecular dimensions.

When pressures are constant and speeds are variable, as at the moment of starting, the coefficient of friction is at its maximum. During standing, the larger part of the lubricant has been squeezed out, and it is only that portion that adheres by virtue of its oiliness that serves as a protection. As speeds increase, there is an abrupt change, and the coefficient of friction reaches its minimum point. At the full speed of the shaft "fluid film" conditions are reached, and the shaft may be regarded as floating in the oil. It is not only necessary to choose a lubricant that will give the least abrasion at slow speeds and heavy loads, but one that will give the least resistance to free movement of the shaft during normal operation of machinery. It is possible to choose a lubricant that will give perfect protection in the range of partial lubrication but whose viscosity is such that a great deal of power is wasted in driving the machinery during the long period of operation. It is better to permit slight abrasion in starting than to put too great a lubricant load on the power plant.

Probably the most important property of lubricating oils is viscosity. Absolute viscosity is a measure of the internal fluid friction. The term "absolute viscosity" has been admirably described by Walker, Lewis, and McAdams ("Principles of Chemical Engineering," second edition, p. 74) in this way. "Assume a large flat trough containing a stationary mass of liquid. If a very large plate having the same density as the fluid be pulled through the mass of liquid in a horizontal plane, it will be found that adjacent layers will start to move, owing to cohesive action between the particles. The particles nearest the moving plane will move more rapidly than those further removed, and hence there is set up a shearing action between the

particles in adjacent planes. When the velocity of a mass of particles of liquid in a plane of unit area and unit distance away from and parallel to the moving plate differs from that of the plate by unity, the force per unit area on the moving plate will be numerically equal to the absolute viscosity." *

The force referred to is measured in dynes per square centimeter, and the unit is known as the "poise" in honor of Poiseuille. This unit is too large for practical use, and the "centipoise" or 0.01 poise is commonly employed. For practical purposes, one centipoise is the viscosity of water at 20° C. Although this unit is used very largely by engineers in connection with fluid flow problems, the viscosities of lubricating oils are usually expressed in terms of the time required for a given volume to flow through the orifice of a conventional instrument known as a viscosimeter.

Stability is perhaps the next most important consideration in a lubricant. In turbines and other machines where the oil is circulated and reused many times, this quality is of great significance. Standardized tests include: the *flash* test, or the temperature at which gases given off the heated oil will ignite; the *fire* test, or the temperature at which the heated oil will burn continuously; the *steam emulsion* test, which is the number of seconds required for a clear separation of the original volume of oil after emulsification by means of steam under arbitrary conditions; and the *carbon residue* (Conradson) test, in which the oil is heated in a crucible enclosed in an outer vessel, and the carbonaceous residue is weighed. As most changes in lubricating oil are the results of oxidation, many empirical tests have been proposed to measure the resistance of oils to changes by oxidation. Generally the conditions surrounding the test are so different from those in actual practice that the results are often misleading. Stability is a very real and important property of lubricating oils, but the precise measurement is a very difficult task.

Harmlessness tests are mainly confined to determination of free acid. No properly made lubricant contains free sulfuric acid, and it is practically impossible for a product insufficiently neutralized and washed to escape rigid refinery supervision. Oils may contain as much as 2% free fatty acids without causing the least harm by corrosion in the presence of water. There are also present in some oils a series of substances called "naphthenic acids," of which little is known. These also are relatively harmless, but in order to avoid question they are usually removed by the addition of caustic soda to the oil during the process of distillation.

* Quotation by permission of The McGraw-Hill Book Co.

It is necessary to know the temperature range through which an oil remains liquid if it is to be exposed to sudden changes in temperature or to continued low temperatures, hence certain mobility tests should be made. Airplane lubricants, car-axle oils, and oils for refrigeration machinery must flow at low temperatures. Such oils require the *pour* test, in course of which the oil is cooled until it is solid, and the temperature noted at which it begins to flow. A number of other tests are applied for purposes of identification and determination of the source of the oil under examination. *Specific gravity* and *color* fall under this category. If animal and vegetable oils (glycerides) are examined, or if mixtures of glycerides and mineral oils are being tested, the usual procedure of determining iodine number, refractive index, saponification number, and similar values is followed.

In general, it may be said that specifications for lubricants are based on a number of factors, chief of which is performance in service, hence it would not be fair or advisable to give values purporting to characterize various kinds of lubricants.

CHAPTER XI

SULFUR AND SULFURIC ACID

SULFUR

Until comparatively recent years the main source of sulfur was volcanic rocks, and most of it came from Sicily. Still another source, which is now of no industrial importance, was by-product sulfur from the Leblanc process for the manufacture of sodium carbonate. In the last twenty years, the sulfur derived from the deposits along the coast of the Gulf of Mexico in Texas and Louisiana has far outstripped in production the material from Sicily. No Sicilian sulfur is imported into this country, and it is estimated that the entire production of Sicily is only 240,000 tons per year. Japan is credited with 60,000 tons and Chile 16,000 tons. The United States in 1929 produced around 2,360,000 tons, of which 95% came from Texas. The sulfur deposits in the United States are located at a considerable depth. The first sulfur produced in Louisiana was under quicksand and other formations which rendered ordinary mining methods entirely impossible. The deposits now being worked are below a caprock of calcium sulfate in a dome formation. The method developed by Hermann Frasch is essentially this. Water heated under pressure to 325° F. by mixing with high-pressure steam is forced down through the annular space between concentric pipes and compressed air through the innermost pipe. The sulfur is melted and brought to the surface by the pressure, separated from air, and cooled in enormous wooden bins, the walls of which are subsequently torn down to permit the removal of the solid sulfur. A part of the hot water is recovered from the deposit by neighboring "bleed wells," passes through heat exchangers, and thus warms up the water which goes to be mixed with steam. By using treated water in high-pressure boilers to generate steam and passing this steam into water from another source, it is possible to use for melting sulfur water that is entirely unfit to go into a boiler. Not more than 2% of the heat actually serves to melt the sulfur. There are considerable mechanical difficulties due either to the settling of the ground around the wells, or to escape of hot water before the sulfur is melted, in spite

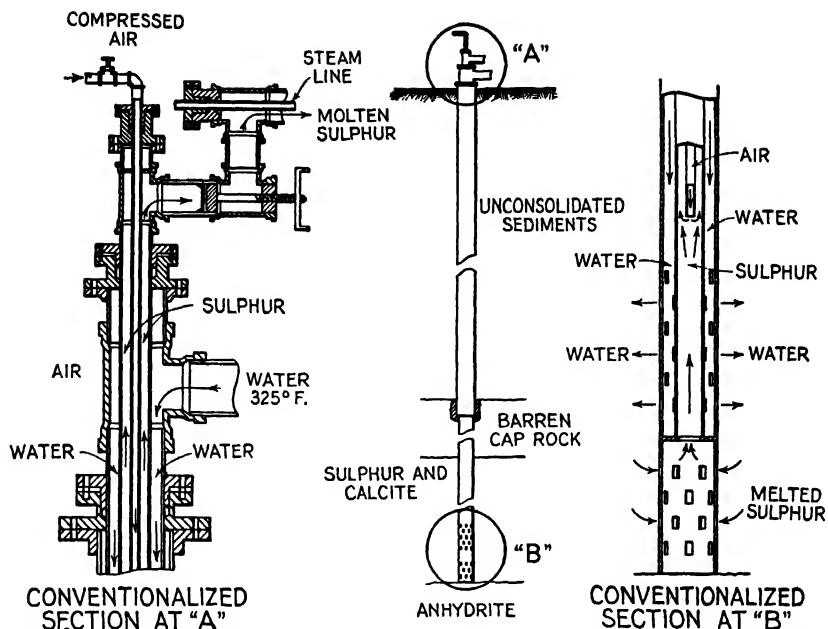


FIG. 61.—Sulfur Well Equipment. Courtesy Texas Gulf Sulphur Company, New York City.

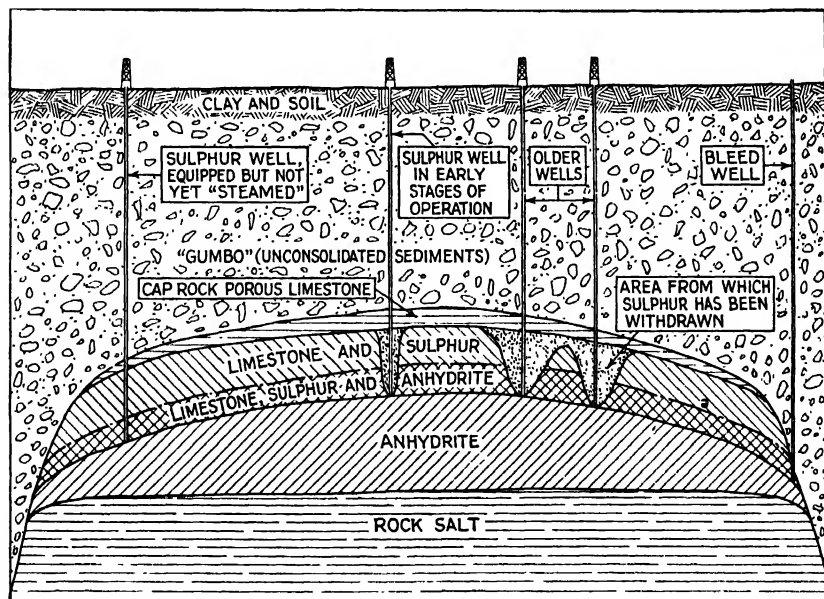
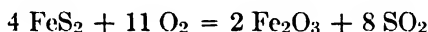


FIG. 62.—Sulfur Salt Dome (Ideal section showing various stages of operation). Courtesy Texas Gulf Sulphur Company, New York City.

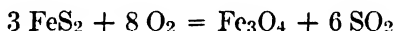
of which sulfur is produced at a relatively low price. The sulfur so obtained is of a very high degree of purity, being something of the order of 99.9%. In order to avoid confusion, this material will be referred to by the common industrial term "brimstone." Sulfur for the most part is converted to sulfur dioxide before it is used industrially. Out of every 100 lb. of sulfur consumed, 89.4 lb. are burned. Of this, 75.4 lb. go to the making of sulfuric acid, and the remaining 14 lb. find use in making the cooking acid (a solution of sulfurous acid and calcium bisulfite) by which wood is made into sulfite process pulp.

SULFUR DIOXIDE

Several mineral sulfides yield sulfur dioxide when burned with air. Pyrrhotite is an important source of sulfur, but that sulfide of iron known as pyrite or pyrites, FeS_2 , is still more commonly used. It burns in air when sufficiently hot according to the reaction



At very high temperatures and with finely divided sulfide the principal reaction is



The residual iron oxide has some use as an iron ore, but the chief value of pyrite lies in the sulfur it contains. The pure sulfide contains 53.4% sulfur and 46.6% iron. The pyrite used in the production of sulfur dioxide is expected to contain as much as 42% sulfur, but lower-grade material may be blended with pyrite higher in sulfur. Among the impurities that may be present are arsenic, copper, zinc, lead, calcium, and magnesium. Some of these retain sulfur in the form of sulfates, and as such remain in the unburned residue; and others, such as zinc, arsenic, and lead, volatilize and contaminate the sulfur dioxide. The process and product largely determine the degree of objectionability of volatile impurities. Since ferric oxide under certain conditions acts as a catalyst to promote the combination of sulfur dioxide and oxygen, some 2% to 5% of the sulfur dioxide is converted to sulfur trioxide. This is a disadvantage in sulfite process paper mills, but is a slight advantage in the lead chamber sulfuric acid process.

Other sulfides such as copper sulfide and zinc sulfide yield gases suitable for use in the manufacture of sulfuric acid. If all the waste gases from copper and zinc smelteries were used in making sulfuric acid, the production would be many times what it is now. The ques-

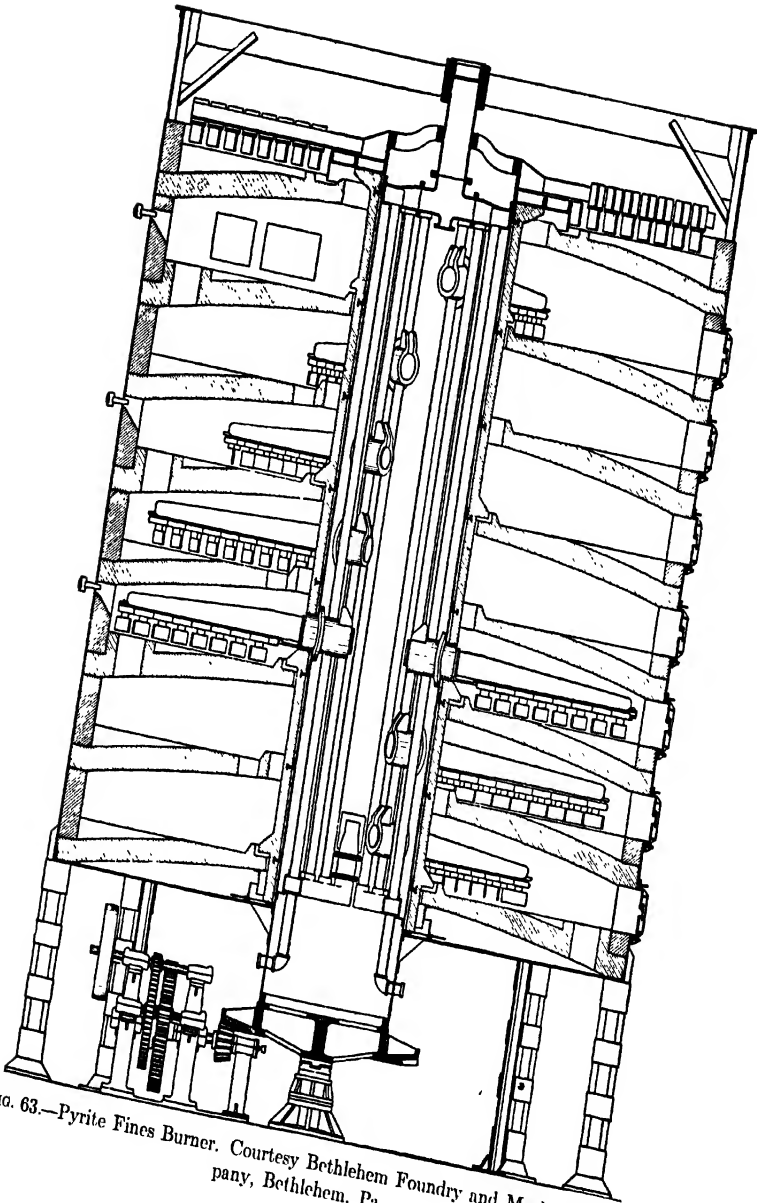


FIG. 63.—Pyrite Fines Burner. Courtesy Bethlehem Foundry and Machine Company, Bethlehem, Pa.

tion of utilizing waste metallurgical gases is largely one of economics, and involves the location of the smelteries, the nature of the surrounding country, the extent of damage done by waste gases, the cost of manufacturing, and the relation of the local demand for sulfuric acid to the supply.

Sulfur dioxide has a limited use as a refrigerant. It is generally prepared as it is needed and used immediately, mainly in the refining of petroleum by the Edeleanu process, the production of sulfurous acid-calcium sulfite solutions in the paper industry, and in the manufacture of sulfuric acid. Liquid sulfur dioxide is used to make hydrosulfides for the textile industry. In producing indigo, sulfur dioxide is the reagent used to make zinc hydrosulfide. In addition to the sulfur dioxide made by the roasting of sulfides, either as the main product or a by-product, the direct combination of oxygen with sulfur is an important method of production. Sulfur dioxide made directly from sulfur is of a high degree of purity, whereas that from burning or roasting sulfides is contaminated with other substances. In some cases, metallic fumes or other impurities must be removed in order to render the gas available for acid manufacture. The two main sources are iron pyrites and brimstone.

Pyrite may be burned with the raw material in the form of lumps, but it is more common practice to crush the pyrite to relatively small size, producing a material known as "fines," and to burn it in a multiple-hearth mechanical furnace. This is a cylindrical shell of firebrick, sheathed in steel, in which are a series of hearths or shelves. Above each hearth move air-cooled radial arms attached to a central shaft, these arms being equipped with stirring blades called "rabblers." The openings that allow the material to drop from one hearth to another are alternately at the center and at the outside, and the rabble blades are so set that the material is alternately raked in a widening or narrowing spiral to the opening. By the time the last hearth is reached, the combustion is practically complete.

In winning copper from sulfide ores by the flotation process a very finely divided pyrite is obtained. This will pass to the extent of 96% through 200 mesh. Its sulfur content is above 50%. It can be roasted in a mechanical furnace, but is best handled in a new type of "flash roaster," regarded by chemical engineers as likely to form the basis for most of the future burning of sulfides. Wet sulfide is first dried in a ball mill by heated air, which sweeps it into a vertical burner. The first atom of sulfur from FeS_2 is driven off and burns to SO_2 . As the residual FeS falls through air fed at the base of the furnace, it

burns to Fe_3O_4 and SO_2 . The high temperature ($1000^\circ\text{C}.$) prevents SO_3 formation. A second chamber removes dust. The gas is quickly cooled in waste heat boilers. The residual Fe_3O_4 is in the form of

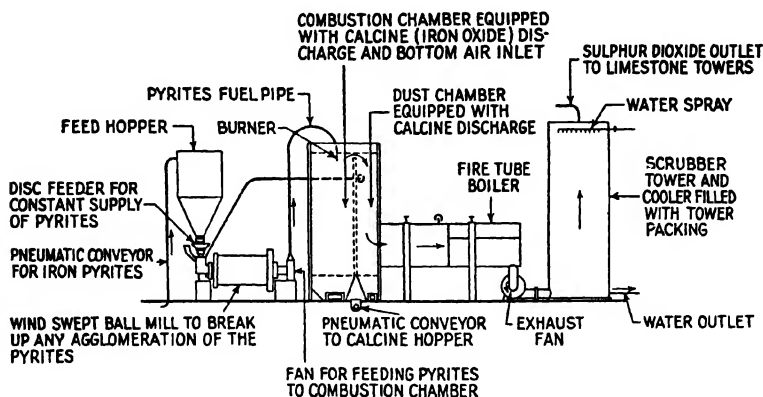


Fig. 64.—Freeman Flash Roaster (for production of sulfur dioxide from pyrite fines). Courtesy Nichols Engineering & Research Corporation, New York City.

thin-walled bubbles, is of a high degree of purity, and is thus a valuable source of iron.

In addition to pan and tray burners, a very widely used burner is

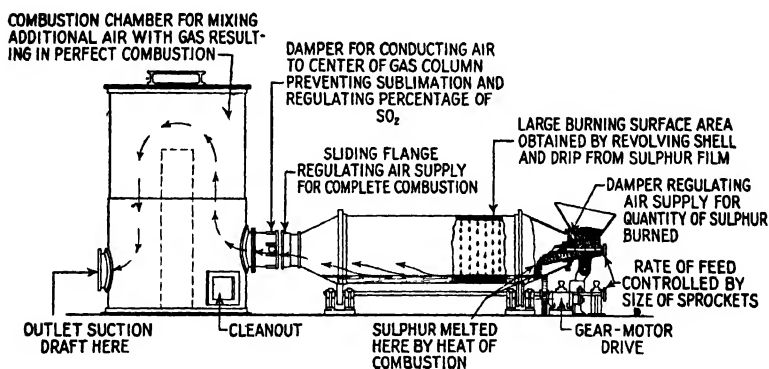


Fig. 65.—Rotary Sulfur Burner. Courtesy Glens Falls Machine Works, Glens Falls, N. Y.

made up of a horizontal rotating cylinder with cone-shaped ends. Sulfur is fed from a hopper at one end, and air is admitted at the same time. The iron of the cylinder is protected by a layer of liquid sulfur.

The gases and some sublimed sulfur pass into a vertical chamber with additional air, where combustion is completed. Quite recently, molten sulfur is being sprayed into a combustion chamber much in the manner of a fuel oil burner, and the hot gases are filtered through towers and sent to waste heat boilers for the production of steam to use in melting the sulfur. The air fed with the sulfur is dried to avoid the elaborate scrubbing and drying operations which are ordinarily necessary. The impurities in Texas brimstone are usually less than 0.1%.

SULFURIC ACID

Sulfuric acid is the most important of all commercial chemicals. It bears the same relation to the chemical industry that steel does to mechanical industries. The majority of chemical products depend at one or more stages of their production on it. In fact, it has been referred to by chemical economists as a barometer of business. Sulfuric acid plants are located near markets for the product, mainly chemical plants, petroleum refineries, and fertilizer manufacturing plants. The production of sulfuric acid in the United States in 1929, according to the U. S. Census, was 8,491,114 short tons in terms of 50° Bé acid, and of this amount 3,000,000 tons were made by the contact process, and the remainder by the lead chamber process.

In 1929 the distribution in terms of 50° sulfuric acid was as follows:

USE	1000 TONS
Fertilizers	2418
Petroleum Refining	1570
Coal Products	935
Chemicals	890
Iron and Steel	800
Non-Ferrous Metallurgy	675
Paints and Pigments	225
Explosives	195
Rayon	150
Other Textiles	90
Miscellaneous	390

Commercial Grades. Sulfuric acid and water mixtures increase in density with increasing amounts of the acid until a maximum of about 95% is reached. At this point the specific gravity comes down so that 93% and 98% have approximately the same density. Consequently the terms shift from density to percentage at 93%. Following are the four common types of acid on the market:

DEGREES BAUMÉ	SPECIFIC GRAVITY, WATER 1	PER CENT SULFURIC ACID
50°	1 53	62 2
60°	1 71	77 7
66°	1 84	93 2

Oleum (solutions of varying strength of sulfur trioxide in sulfuric acid).

Sulfuric acid is capable of dissolving sulfur trioxide up to very high concentrations, dilute solutions being liquid at ordinary temperature and more concentrated solutions solid. When sulfur trioxide-sulfuric acid solutions are mixed with water, the oxide combines with the water to form sulfuric acid. There are two methods of designating the strength of solutions of sulfur trioxide in sulfuric acid: percentage of dissolved sulfur trioxide; and the percentage of the original weight of the oleum which can be made into 100% sulfuric acid by adding water. Thus 20% oleum may also be called 104.5% sulfuric acid.

The variations in freezing point of sulfuric acid solutions are no doubt due to the formation of stable hydrates, since the freezing point curve corresponds in form to that of a salt which has several hydrates. The following data taken from Pictet will show the variation of freezing points with concentration:

MOLS H ₂ O PER MOL H ₂ SO ₄	PER CENT H ₂ SO ₄	SPECIFIC GRAVITY	FREEZING POINT
0	100 00	1 842	+10° C.
1	84 48	1 777	+ 3° C.
2	73 08	1 650	-70° C.
10	35 25	1 268	-88° C.
20	21 40	1 157	-17° C.
50	9 82	1 067	- 3 5° C.
100	5 16	1 032	+ 2 5° C.

I. The Contact Process

The chief difficulty of any process lies in the conversion of sulfur with a positive valence of 4 to sulfur with a positive valence of 6. An understanding of the contact process depends upon a thorough consideration of the following equilibrium:



The reaction takes place so slowly in the absence of a catalyst as to be commercially unprofitable. A catalyst for the conversion of sulfur dioxide to sulfur trioxide, to be efficient, must be able to effect this conversion rapidly at a temperature that permits the existence of a high equilibrium concentration of sulfur trioxide. The most favorable practical conversion temperatures are from 425° C. to 450° C. Above 450° C. the equilibrium concentration of sulfur trioxide falls rapidly. At 500° C. the percentage of sulfur trioxide that can theoretically exist in equilibrium with sulfur dioxide is about 93.

Two types of catalyst are effective in the favorable range: finely divided platinum on the surface of some inert material such as magnesium sulfate, asbestos, or silica gel; and complex non-siliceous vanadium compounds of the "base-exchange type" in which the vanadium is in the non-exchangeable portion. Iron oxide is mechanically a good catalyst, but at 600° C. is able to effect a conversion of only about 40% to 50%.

The production of sulfur trioxide is an exothermic reaction. Common practice is to utilize the heat of reaction to bring the entering gases to the desired temperature, and to use the cold gases to hold down the temperature in the contact chamber. This is carried out on the counter-current principle by the use of heat exchangers. These may be separate or combined with the converters.

The general process of making sulfuric acid known as the contact process may be divided for purposes of explanation into the following steps.

Preparation of Sulfur Dioxide. This has already been fully discussed. It should be noted that for the contact process sulfur dioxide is best prepared by the burning of relatively pure sulfur, since the gas made from pyrite is more difficult to purify.

Purification of Gases. Since catalysts are impaired by contact with dust, moisture, and other impurities, it is necessary to purify the gases very thoroughly before they pass to the converters. This purification generally includes cooling, scrubbing, filtration, and drying.

The gases from sulfur burners are cooled in horizontal lead flues, which are either sprayed or immersed in tanks of water; in vertical lead pipes sprayed with water; in vertical, air-cooled, cast-iron pipes; and towers packed with acid-proof material down which dilute sulfuric acid is passed. This last-named method combines cooling and concentration of weak acid. Tower systems scrub, but are regarded as offering some complications in the way of cooling the recirculated acid.

The presence of sulfur trioxide in the gases along with water vapor renders the use of iron impossible, and acid-proof brick in towers is necessary. For the satisfactory removal of chlorine from the gases it is necessary to use 30° sulfuric acid.

The production of sulfur dioxide gas, regardless of its source and its subsequent cooling, produces a true mist, the removal of which represents the most difficult problem in the purification step of a contact plant. The gas leaving the purification system should contain less than 0.006 mg. sulfuric acid mist per cubic foot of gas. If this mist is properly removed, such impurities as arsenic, which are apt to attach themselves to the small acid particles, will also be eliminated. This mist is removed either by very large lead-lined boxes packed with coke ranging from 6 or 8 mesh at the bottom to 30 mesh at the top, or by electrostatic precipitation.

The amount of water left in the gases is determined by the concentration of sulfuric acid in the drying towers. Some manufacturers finish the gases with 80% sulfuric acid; others use from 98% to 99%, maintaining this concentration by adding oleum. Chamber acid must not be used at this stage because of the danger of carrying arsenic to the converters. The usual form of dryer is a tower packed with quartz through which the drying acid is passed counter current to the gases. By this time the removal of particles in colloidal suspension is so complete that there is no Tyndall effect.

A plant described at the June 1931 meeting of the American Institute of Chemical Engineers and referred to as a "raw gas vanadium contact plant" is regarded as an outstanding development in sulfuric acid manufacture. The plant in actual operation at the time of the reading of the paper had a capacity of 50,000 lb. of sulfur per day. The sulfur is melted by steam coils in brick-lined pits, impurities accumulated in shipment being allowed to settle. Molten sulfur is run into a large, vertical, steel cylinder lined with firebrick, equipped with plates, pyramids, and arches, and burned with clean, dry air. The gases are first cooled in a jacketed cast-iron shell, air being blown through the annular space, and thence pass to tubular coolers employing air. The hot air is used in water heaters. Final protection against dust is afforded by a filter packed with a granular material. The gases are thus delivered at the desired temperature to converters containing vanadium mass.

Gas Conversion. All systems have provisions for preheating the gases which in most plants are merely supplementary. Practically all preheaters are boiler tubes set in a furnace. Most preheating is done

in heat exchangers of the same type of construction as surface condensers.

Ferric oxide is usually handled in a shaft of 20 to 25 ft. area and 10 to 12 ft. in height, provided with a grate which supports the screened cinder from pyrite burners. Since considerable heat develops in the reaction, gas pipes may be carried through it, the converter thus functioning as a preheater.

The converters in which platinum or vanadium catalysts are used have heat exchangers either as a part of the converter (regenerative),

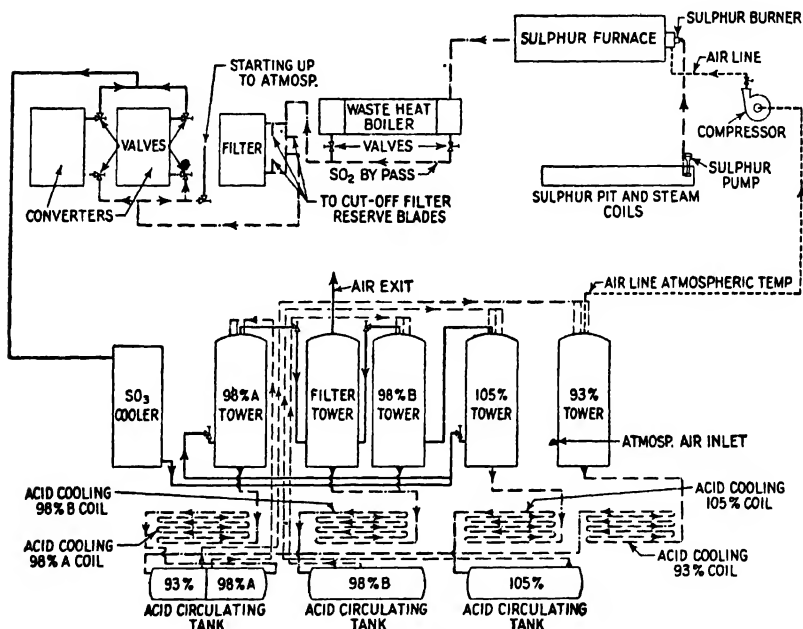


Fig. 66.—Contact Sulfuric Acid Plant. Courtesy Chemical Construction Corporation, Charlotte, N. C.

or separate and distinct from the converter (non-regenerative). Regenerative heating may be accomplished by having a double-walled space through which the gases pass before they enter the inner shell in which the catalyst rests on shelves, or by packing the catalyst in tubes around which the gases pass before entering. Still another method is to introduce the gases by means of inner tubes into tubes closed at one end, around which the catalyst is packed, thus permitting them to take up heat from the catalyst mass before reaching it. In one type of converter, bars and pyramids of cast iron serve as heat

reservoirs, taking up heat from the catalyst mass and conveying it to the entering gases. A non-regenerative converter is a well-insulated shell in which are a series of shelves supporting the catalyst mass. Platinum catalyst is prepared by applying platinic chloride to calcined magnesium sulfate, asbestos, or silica gel, and converting the salt to platinum by direct heat or reducing agents. A very effective method of handling the catalyst is to distribute it on small pellets of the carrier material.

In one system, sulfur dioxide is oxidized in two stages in two converters equipped with two heat exchangers each connected in series. The cold sulfur dioxide gas from the drying tower enters heat exchanger No. 1 and then passes to heat exchanger No. 2, thereby becoming heated to the desired conversion temperature. The heated gas then enters converter No. 1, wherein partial conversion takes place and the gas mixture becomes heated beyond the desirable maximum for good conversion. The partially oxidized gases then pass to heat exchanger No. 2, in which the excess heat is lost to the incoming gas. The partially converted gas, now cooled to a temperature favorable for conversion, enters converter No. 2 for the second conversion stage, and the temperature of the gas again rises, though not as high as in No. 1. The converted gas, with about 96% of the sulfur dioxide now oxidized to sulfur trioxide, is conveyed to heat exchanger No. 1, where it transfers heat to the cold entering gases.

Cooling Gases from Converter. In addition to the use of heat exchangers, pipes cooled by natural air draft may be employed for the purpose of reducing the temperature of the gases before they go to the absorption system. If the gases have not been previously well dried, these coolers are subject to corrosion by virtue of the condensation of sulfuric acid. For dry gases, steel is preferred, since cast iron is in danger of cracking.

Absorption. Since water vapor diffusing into bubbles of gas containing only a few per cent of sulfur trioxide forms droplets of sulfuric acid surrounded by gas films, it is necessary to use concentrated sulfuric acid, which has a negligible water vapor pressure, for absorption of gases. The gases may be passed through 100% sulfuric acid until the desired concentration of oleum is obtained. Ordinarily the sulfur trioxide gas passes through several absorption towers in series, the final one being fed with acid of 98.5% to 99% sulfuric acid content. The reaction is strongly exothermic, and increasing temperature means less absorption, as well as mist formation. Therefore the circulating acid must pass through coolers.

If oleum is desired, there may be a series of towers so that decreasing strengths are produced in each in succession; or a single oleum tower may be used, followed by a final tower in which monohydrate sulfuric acid is produced. In any case where 100% or stronger acid is made, there is some sulfur trioxide in the exit gases. Oleum towers are tall and narrow, lined with a special type of brick, and packed with quartz. The top and bottom may be of cast iron, but this and all steel used in construction must be carefully protected by brick. The acid is sprayed in at the top of each tower, and meets the gas counter current.

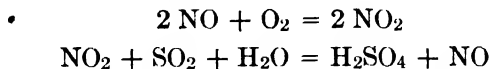
A properly operated plant may be run for years without any change, alteration, or loss of catalyst, if the raw material is brimstone. If the raw material burned is pyrite or other sulfide ore, the platinum mass may gradually suffer deterioration in conversion efficiency, and in case of active poisoning by arsenic or other impurities may have to be regenerated as often as once a year. Vanadium mass is susceptible to damage by fluorine, moisture, and dust particles in the gases.

II. The Lead Chamber Process

The older method of making sulfuric acid involves the use of oxides of nitrogen as carriers of oxygen in order to bring about the conversion of sulfur with a positive valence of 4 to that with 6. The essential steps in this process are:

- (a) Oxidation of sulfur to sulfur dioxide with excess air.
- (b) Addition of water and oxides of nitrogen.
- (c) Oxidation of sulfur with a positive valence of 4 to a positive valence of 6, through the formation and subsequent decomposition of intermediate products, with the final formation of sulfuric acid.
- (d) Recovery of the oxides of nitrogen by absorption in strong sulfuric acid.

The simplest explanation of the lead chamber process is given by the following cycle of reactions:



These reactions, however, do not account for the absorption of the oxides of nitrogen in sulfuric acid for the purpose of returning them to the system. Nitric oxide is not absorbed at all in concentrated sulfuric acid, and nitrogen tetroxide is absorbed only very slowly. The oxygen carrier that actually functions is usually spoken of as nitrogen trioxide, N_2O_3 , but is an equimolecular mixture of the nitric oxide and nitrogen

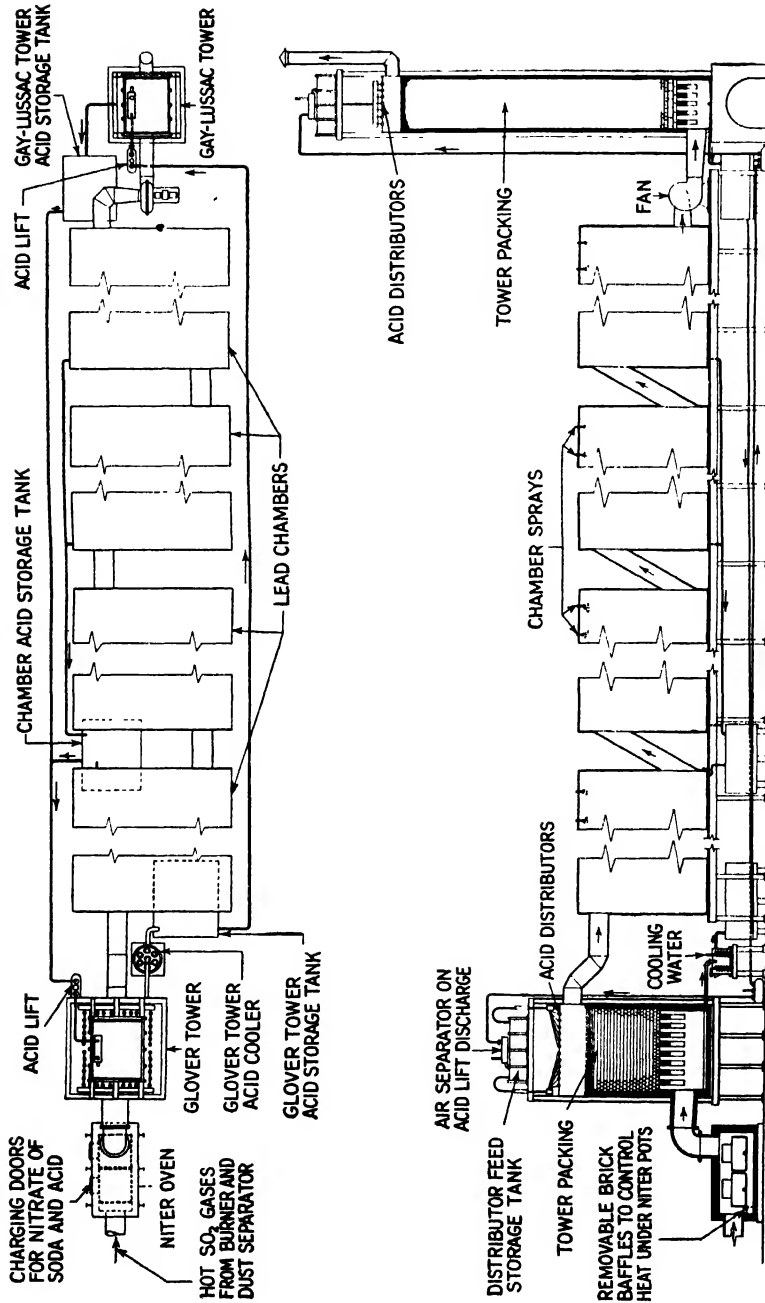
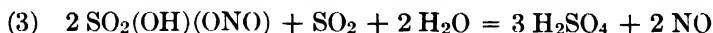
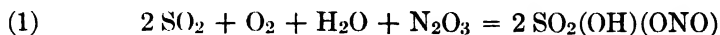


Fig. 67.—Lead Chamber Sulfuric Acid Plant—Plan and Elevation. Courtesy Mr. Osborne Bezanson, Merrimac Chemical Company, Boston, Mass.

dioxide. For purposes of simplification it may still be written N_2O_3 instead of $\text{NO} + \text{NO}_2$, assuming that small amounts of nitrogen trioxide are formed as rapidly as used up. Although the reactions are probably quite complex, the following accounts satisfactorily for what takes place in each part of the plant:



Reactions (1) and (2) represent a summation of effects. The oxide in the first chamber is predominantly nitric oxide, since the conditions are primarily reducing. When a small amount of nitric oxide is oxidized to nitrogen dioxide, the two form nitrogen trioxide, which is immediately converted according to Reaction (1) to nitrosyl sulfuric acid. Reaction (3) accounts for the decomposition at higher temperatures in the middle of the Glover tower of nitrosyl sulfuric acid which escaped hydrolysis farther up in the tower.

The gases from sulfur burners require no purification, but various dust settling or collecting devices are commonly employed with pyrite burners.

Glover (Hot) Tower. The flue from the furnace is connected to the base of a large lead-covered tower of square or circular cross section, lined with acid-proof brick, the flue entering at the side near the base. This tower in a plant of moderate capacity is from 10 to 15 ft. in diameter and from 30 to 40 ft. high. At its base is a brick-lined lead pan somewhat larger in diameter than the tower. The base of the tower is from 10 to 15 ft. above the ground level to permit gravity flow of acid discharged from the tower into acid coolers. Heavy arches built up within the tower support the packing, now commonly acid-proof brick of various shapes. There is a certain amount of unpacked space at the bottom to permit distribution of gases, and there is also some empty space above the packing at the top of the tower. In the top are a large number of acid-sealed inlet holes, which serve to distribute the acid over the packing material.

Chambers. A series of chambers are connected by a flue with the top of the hot tower. These are essentially enormous rooms made of heavy sheet lead. The lead is held to a surrounding wooden or steel framework by lead strips burned on the walls and top. The chambers are commonly enclosed in buildings, which are equipped with windows for ventilation and temperature control. The number of chambers is

rarely less than four or more than twelve. Their height is usually from 20 to 30 ft., their width approximately the same, and their length from 50 to 150 ft. The average cubical capacity in this country is around 14 cu. ft. per pound of sulfur burned per 24 hours. Water is added to the chambers in the form of a spray by means of atomizers. Drip pipes burned to the outside of the chamber walls about 4 ft. from the ground permit the continuous discharge of a "drip" of the acid being made inside the chamber. This drip collects in a lead drip cup placed beneath the spout of the drip pipe. The specific gravity of the collected drip is tested at frequent intervals by means of a hydrometer, and these specific gravity tests are used by the operator for the control of the amount of water admitted through the atomizers to the chambers. Draft is produced partly by the natural pull of a stack discharge of warm gases into the cooler atmosphere, and partly by a fan.

Some modifications of the simple chamber system are meeting with considerable success. A single-chamber plant has found very limited use in this country, this chamber being of the order of 70 ft. in height. A chamber of the general form of a truncated cone permits the flow of water over the outside surface and is said to have reduced necessary chamber space to around one-third that required by the ordinary plant. In another system the first chamber is large, and is connected with a packed tower for recirculation. Intermediate towers function primarily to remove mists, which take up the oxides of nitrogen. The hot tower may discharge its gases through long lead boxes in which corrugated lead rollers revolve at high speed to form an acid spray. Where the cost of lead burning is excessively high and a material for making acid-proof brick is a by-product of mining operations, sulfuric acid plants have been built in which a series of packed cells or towers have taken the place of ordinary lead chambers. Such cells are sheathed with lead to prevent leakage, but require very much less lead than open chambers. A tower chamber is being used abroad which consists of a tall chamber at the top of which is a disperser producing an acid mist and uniform distribution of a layer of liquid acid on the inside of the walls. Water sprays are thus eliminated. The temperature of the circulating acid in the first two chambers is lowered by passage through acid coolers. These chambers are said to be very effective in terms of chamber space. In all cases, the chambers or towers serve mainly as enclosed spaces within which the reactions take place, and as a means of dispersing the heat of reaction.

Gay-Lussac (Cold) Towers. These towers are of essentially the same type of construction as the hot tower, but are not so rugged, their

function being to handle cool gases. In order to get the tower tops, both hot and cold, on the same operating level, it is common practice to use more than one cold tower. The first tower is connected to the last chamber by a flue, and at the top of the last tower is an exit stack fitted with a side tube covered by a glass bell, so that the color of the exit gases may be observed. Acid-proof ceramic packing material is used.

Miscellaneous Equipment. A lead chamber plant is also equipped with storage tanks, acid coolers, and acid pumps of various types, including air lifts, automatic or hand-operated blow-cases, and centrifugal pumps.

The production of sulfuric acid by the lead chamber process can best be understood by dividing the process into three streams. Two of these may be regarded as an unidirectional flow, and the third as a cycle.

Gas Stream. Sulfur dioxide and oxygen from the excess air, together with residual nitrogen, come from the burners and pass in at the base of the hot tower. Gases from pyrite burners will contain around 7.5% sulfur dioxide, and brimstone burner gas commonly carries as much as 10%. The gases are quite hot, and must be cooled before they are allowed to go into the chambers. This is accomplished by passing 60% sulfuric acid, which is a product of the chambers, down the Glover tower against the gases. Water is removed from this acid until it reaches a concentration of 75% to 78%. This water constitutes the third necessary ingredient as shown by Reaction (1). As the gases pass into the upper part of the tower, they pick up nitrogen trioxide, which has been liberated from the nitrous vitriol supplied from the final Gay-Lussac tower. Reaction (2) and further down Reaction (3) bring about this result. From 15% to 25% of the oxidation of sulfur dioxide takes place in the Glover tower. The gases, which now contain the four essential substances shown in Reaction (1), pass into the chambers. Reactions (1) and (2) go on side by side, being repeated a countless number of times. If too little water is present, crystals of nitrosyl sulfuric acid collect on the lead, and finally decompose to give nitric acid and cause corrosion. Too much water also leads to the formation of nitric acid, but by a different mechanism. Finally the quantity of sulfur dioxide has been reduced to a small amount necessary to prevent the formation of nitric acid and consequent corrosion of lead, and also enough to prevent oxidation of nitric oxide to nitrogen dioxide beyond the equimolecular quantities. Any excess of either component above the proportion necessary to produce

nitrogen trioxide involves a loss of "niter" in the form of recoverable nitrogen oxides. If the sulfur dioxide is completely used up before the gases reach the cold tower, the necessary amount can be taken from the first chamber and supplied to the tower by a fan. If there is too little oxygen, nitric oxide remains in excess and is lost. A deficiency of niter means not only loss of sulfur dioxide, but also loss of niter and formation of nitric acid. It is necessary to recover the oxides of nitrogen. The gases pass into the base of the cold tower and meet a stream of 78% sulfuric acid. Here Reaction (2) takes place, going to the left with the formation of nitrosyl sulfuric acid and water. The nitrosyl sulfuric acid is dissolved in the scrubbing acid, and this solution is known as "nitrous vitriol." The spent air passes out at the stack. There are inevitable small losses caused by incomplete reactions and by a lack of balance between nitrogen dioxide and nitric oxide.

Product Sulfuric Acid Stream. The sulfuric acid formed in the chambers by Reaction (1) settles as a fine rain to the bottom of the chambers, or condenses and drips down the inner surface of the walls, and collects on the floor pans. This acid is approximately 60% in concentration. When acids of this strength or weaker are desired, the product may be removed from the process. However, the demand as a rule is for a stronger acid, and there is a great excess of heat in the burner gases which must be removed before they reach the chambers. Consequently, it is possible to use this dilute acid to cool the burner gases in the hot tower, and at the same time the acid itself is concentrated by the evaporation of the water, which is needed in the chambers. Hence the acid from the chambers is commonly removed to the top of the hot tower and mixed inside the Glover tower with the nitrous vitriol from the Gay-Lussac tower. Water also may be added if necessary. As soon as the mixed acids encounter the hot sulfurous gases the oxides of nitrogen are removed, first by Reaction (1) and later Reaction (3). The nitrogen-free acid passes down, and is further concentrated by evaporation. The heated acid is passed through coolers and sent to storage tanks. This acid is from 59° to 60° Bé in strength.

Catalyst Recovery Stream. It is estimated that something like 3 tons of acid must be kept in circulation for every ton of acid made. A portion of the acid from the coolers is sent to the top of the cold tower. As it passes down the cold tower it picks up the oxides of nitrogen in the form of nitrosyl sulfuric acid and becomes the "nitrous vitriol" previously referred to. In terms of nitrogen trioxide its con-

centration is between 1% and 1.5%, which is equivalent to an average concentration of 3% in terms of sodium nitrate. This is removed to the top of the hot tower, mixed with chamber acid, and water, if necessary, is denitrated by the combined effect of water, heat, and sulfur dioxide, and is drawn off at the base of the hot tower as a part of the product stream. This acid circulates continuously in a cycle for the purpose of recovery of nitrogen oxides.

Compensation for Niter Loss. A certain amount of loss of nitrogen oxides is inevitable, owing to incomplete reactions and loss of proper balance of the oxides of nitrogen. This is commonly calculated in terms of pounds of sodium nitrate per 100 lb. of sulfur burned. The make-up material may be as low as 2 lb. sodium nitrate per 100 lb. of sulfur, commonly averages 4 lb., and in some special cases is as high as 8 lb. The most modern method of compensation for losses, which is now in general use and which has been made possible by the development of cheap methods of producing ammonia synthetically from its elements, is to pass nitric oxide derived from the catalytic oxidation of ammonia directly and continuously into the flue between the top of the Glover tower and the first chamber.

Control of Process. Aside from the ordinary laboratory tests on raw materials and products to determine commercial quality, the lead chamber process is regulated and controlled by relatively simple tests. The specific gravity of the acid from chamber drips and from the towers is continuously shown by hydrometers in overflowing cylinders. The amount of nitrogen compounds in the acid from the cold tower is determined at intervals. Temperatures at different points are continually noted, and usually automatically recorded. The color of the gases which escape from the cold tower is watched. An important control of the chamber process is the color of the gases as they leave the last chamber just before entering the Gay-Lussac tower. Still another method used in some plants is to determine the ratio between the concentrations of sulfur dioxide in the gas entering the hot tower and in that taken from several points in the chambers, this ratio being correlated with the quantity of nitrogen oxides used.

Functions of Equipment. The functions of pumps, storage tanks, and coolers are obvious. The hot tower serves to denitrate nitrous vitriol, to concentrate chamber acid, to cool and clean the gases, to provide make-up catalyst, and to a partial extent at least to produce acid. In this connection it may be noted that the use of the hot tower as a concentrating first tower does not permit the production of acid stronger than 78% without some disadvantage of inflexibility of con-

trol. The chambers serve to afford reaction, cooling, and condensation space. This is also true of intermediate towers. The cold tower has as its sole function the recovery of nitrogen oxides.

Purification of Chamber Acid. Acid equal in purity to that made in the average contact plant may be obtained from the middle chambers of a chamber plant. The back chamber generally contains so much niter that its acid cannot be used. For some purposes the acid made in the front chambers or in the Glover tower of a chamber plant is not satisfactory unless it is subjected to partial purification, which process, however, is so expensive that it is seldom employed. The most objectionable component is arsenic.

Concentration of Chamber Acids. For many purposes a stronger acid than that produced by the hot tower is desired. The most common method now employed is that of tower concentration. The acid to be concentrated is fed in at the top of a tower made of refractory material and packed with quartz. Hot gases from burning oil are passed up counter-current through the tower. The concentrated acid is run through coolers and is ready for market. This process results in a certain amount of entrainment. A part of the liquid carried out by the gases may be removed by filtration. Electrical precipitation is very commonly used to remove true mists from the exit gases.

Comparison of Contact and Lead Chamber Processes. When a very pure and highly concentrated acid is required, the contact process is distinctly superior to the older method. It is also the only way in which oleum (fuming sulfuric acid containing SO_3) is satisfactorily prepared. It requires little labor, but highly skilled manipulation and supervision are necessary. The initial cost of a contact plant is relatively high, primarily because of the expensive catalyst and the complicated purification system. Where an acid not exceeding 93% H_2SO_4 is required, and no very rigid standards of purity are demanded, the lead chamber process still predominates. The construction of the chamber plant is simple, there is comparatively little deterioration, and the labor required is in the main not skilled. The lead chamber process is particularly useful in making sulfuric acid for the manufacture of acid phosphate, since this requires no stronger acid than 67%. Each process occupies a distinct field of its own, and there is no immediate prospect of the contact process completely supplanting the older method of manufacture, although in this country the percentage of product that is made by the contact process has been gradually increasing.

CHAPTER XII

FIXED NITROGEN

Although the term "fixed nitrogen" is commonly thought of as applying to compounds that can be assimilated by plants, it refers broadly to all compounds of nitrogen. The naturally occurring compounds of carbon, hydrogen, oxygen, and nitrogen, known as proteins, will be considered later in connection with glue, casein, silk, wool, and leather. This chapter is concerned with the production of ammonia, cyanamide, cyanides, the oxides, and the oxygen acids of nitrogen, and their uses in industry.

Of all the uses of nitrogen compounds, the most important is plant food, about 70% being applied to the soil in fertilizers; the remaining 30% finds use in various industries. In modern intensive agriculture three elements are removed from the soil more rapidly by drainage and harvesting of crops than they can be replaced by natural means. These are phosphorus, potassium, and nitrogen. There are enormous deposits of phosphorus and potassium compounds that are assimilable plant foods. The nitrogen cycle in nature may be regarded as beginning with the plant, which takes nitrogen compounds from the soil and uses them in its growth and development. If the plant matures and dies, the nitrogen is returned, to be used again by other plants. If the plant is eaten by animals, the nitrogen ultimately returns to the soil both in products of metabolism and in the bodies of the animals after their death. Under conditions of a more primitive civilization, soil bacteria could take up atmospheric nitrogen and convert it into compounds that plants use rapidly enough to supplement the removal and waste of nitrogen compounds. Modern agricultural conditions and segregation of population in the cities have upset this cycle, and the demand for nitrogen far exceeds that supplied by natural agencies.

Late in the last century Sir William Crookes warned that when the Chilean nitrate beds were exhausted the world would face starvation because of a lack of fixed nitrogen. As a result of the work inspired by this idea, the world is practically independent of natural nitrate deposits. However, this source is being widely used, and by-product

nitrogen compounds from the distillation of coal are of great importance. At the same time, all the world's fixed nitrogen market could be supplied by expansion in production of chemical plants using known methods of converting atmospheric nitrogen into available forms.

Higher animals may live for a considerable length of time without carbohydrates and fats, but omission of proteins from the dietary means starvation. When it is remembered that about one-sixth of protein is nitrogen, the fixed nitrogen industry becomes to everyone a matter of vast social, economic, political, and personal importance.

The average amount of nitrogen in air is 78%. Commercial nitrogen contains argon, since this is present in air to the extent of nearly 1%, and also very small amounts of other gases all of which are calculated as nitrogen in combustion reactions. Pure nitrogen can be made by decomposition of nitrides, but for most industrial purposes it is not necessary to remove argon. There are two general methods of obtaining nitrogen for industrial use in nitrogen fixation processes. One is a physical method depending on fractional distillation of liquid air, and the other is a chemical method in which the reactive components of the air are removed by combination and absorption.

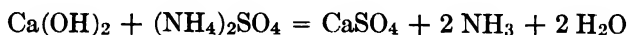
Nitrogen boils at -195°C . (78°K ., absolute temperature on the Centigrade scale); oxygen is less volatile, boiling at -182°C . (91°K .). This difference is sufficient to produce, in a single distillation with a bubbling plate column, either pure nitrogen or pure oxygen. Air is scrubbed free of carbon dioxide, compressed, cooled, and allowed to expand. This expansion produces partial liquefaction. The liquid is fed at the proper plate of the column, and as it runs down from plate to plate it meets an ascending stream of a very cold nitrogen-oxygen mixture. Practically pure nitrogen escapes from the top, where a portion is condensed and refluxed, the remainder passing through heat exchangers and to storage.

In the modern chemical method, incandescent coke is used to remove the oxygen of the air. The synthesis of ammonia requires three volumes of hydrogen for each volume of nitrogen. The synthetic ammonia processes are the only ones using nitrogen from the blast gases of the water-gas process. Hence its preparation by this method will be described in connection with hydrogen production.

Ammonia and Ammonium Salts. There are two main sources of ammonia and ammonium salts: coal and atmospheric nitrogen.

Ammonia from Coal. Coal is destructively distilled in retorts and ovens in order to get metallurgical coke and coal gas. In the purification of the gas a number of by-products are obtained, among them a

variety of ammonium compounds and gaseous ammonia. When water scrubbing is used, the solution of ammonia and ammonium compounds is fed into a fractionating column attached to a still. The steam in the column drives gaseous ammonia out of solution and also breaks up the ammonium salts of weak acids such as carbonate and sulfide. Ammonium sulfate and chloride are decomposed by the action of lime in the still.



The resulting product is marketed as "aqua ammonia," or a solution containing 28.5% ammonia with a specific gravity of 0.90. Anhydrous ammonia can be readily obtained by distilling the gas from this solution, and drying, cooling, and compressing until a liquid results, which is handled in cylinders.

By-Product Ammonium Sulfate. In the "hot process" for ammonium sulfate, the ammoniacal liquor, which is a water solution of ammonium compounds separated from the tar collected in the mains and condensers, is distilled with the aid of lime. The resulting gaseous ammonia is added to the partially purified coal gas, which still carries considerable amounts of ammonia; the mixture is warmed and is bubbled through a saturated solution of ammonium sulfate to which free sulfuric acid is continually added. Crystals of ammonium sulfate constantly separate, and at intervals the solids are scraped into a centrifugal and freed from adhering solution. In a number of plants all the ammonia is scrubbed out of the gas by water, the resulting solution is run through a lime still, and the concentrated gas is converted to ammonium sulfate in a smaller type of saturator by means of sulfuric acid.

Not more than 20% of the nitrogen in coal is recovered from coal gas. Since only 5 to 8 lb. of fixed nitrogen are obtained from each ton of coal carbonized, it is obvious that this nitrogen may be regarded purely as a by-product of the coke and gas industries. These industries in turn depend on the markets for gaseous fuel, pig iron, and steel. Although a hundred billion tons of fixed nitrogen could be obtained by the destructive distillation of the world's supplies of coal, this nitrogen will become available only as the coal is needed for making coke and gas. Modern industry uses vastly more coal directly as fuel than it distills, the result being the total loss of the nitrogen.

Synthetic Ammonia. A study of the equilibrium, $\text{N}_2 + \text{H}_2 \rightleftharpoons 2 \text{NH}_3$, +24,000 calories, indicates that pressure increases the amount of

ammonia formed, since four volumes are reduced to two. The speed of attainment of equilibrium is greater the higher the temperature, but the effect of increased temperature here is to shift the equilibrium towards lesser yields of ammonia. In actual practice, the time allowed for passage of the gases is not sufficient for equilibrium to be reached, and under certain conditions increase in temperature will actually increase the yield. Catalysts have been developed that will greatly increase the speed of equilibrium attainment. Pressures of 1500 to 15,000 lb. per square inch are required. The temperature found most satisfactory is around 500°C ., but in practice the range is from 450° to 700°C . The catalyst most commonly employed is a spongy iron containing small amounts of aluminum and potassium as "promoters." The yields of ammonia vary with pressure as well as with the length of time the gases remain in contact with the catalyst mass. It is not always profitable to take the time necessary for a reaction to reach equilibrium. The highest recorded yield of ammonia is around 65% at the pressure of 15,000 lb. and with complete equilibrium, but in practice under these conditions the yield is rarely over 50%. The average yields are from 5% to 15% at pressures of 3000 lb. The energy required to compress gases is not a simple straight-line function of pressure, since at very high pressures the effect of molecular attraction is correspondingly great. The limiting factors are the strength of the apparatus and the ability to make gas-tight fittings and connections. Development of such high-pressure equipment is regarded as a major engineering achievement, and the synthetic ammonia industry has paved the way for a number of other processes of great industrial significance and importance. Among these are the synthesis of methanol and the hydrogenation of coal and petroleum. Following are the important steps in the synthesis of ammonia.

1. *Preparation of Hydrogen and Nitrogen.* The most difficult, expensive, and important part of the whole process of ammonia synthesis is the production of hydrogen. Hydrogen may be separated from coke-oven gas largely by a complicated system of liquefaction by means of liquid nitrogen, with the removal of all products but hydrogen. The separated components are valuable not only as fuel but also as the raw material for chemical industries. Natural gas, which is composed mainly of methane with smaller amounts of ethane, is also a source of hydrogen, the gas being decomposed at a high temperature to carbon and hydrogen. Electrolytic hydrogen is quite pure, but practicable only where the cost of current is very low, or where considerable quantities of off-peak current are available. There is some

promise of by-product hydrogen from the manufacture of phosphoric acid by the action of steam on phosphorus. Certain fermentation processes and the alkali-chlorine industry also have by-product hydrogen to dispose of.

Since more hydrogen is made from water gas than from all other sources combined, probably to the extent of three-fourths of the entire production, this process is selected for description. Both nitrogen and hydrogen are obtained in the same operation. Anthracite coal or coke is used as fuel in the generator of a water-gas set, which is arranged for the manufacture of "blue gas" alone. (See Chapter XXIV, Coal Products.) More than half of the resulting blast gas is nitrogen. After a brief period of blasting, the air is cut off and steam is passed through the fuel bed. The main water-gas reaction is $C + H_2O \rightleftharpoons CO + H_2$, 39,300 calories. Some carbon dioxide is formed at the same time. The blast gas and water gas are mixed in such proportions as to give a final product with three volumes of hydrogen to one of nitrogen, which means about two volumes of water gas to one volume of blast gas. The removal of carbon monoxide is the chief difficulty in this process. Most of this component is eliminated through oxidation by means of steam to carbon dioxide with the simultaneous formation of hydrogen. At 500° C. the equilibrium is $CO + H_2O \rightleftharpoons CO_2 + H_2$, 10,000 calories. The catalyst used is ferrous oxide. The mixed gases are saturated in scrubbing towers fed with hot water, and additional steam is added. After further warming in heat exchangers, the gases pass into the converters, where they come in contact with the catalytic mass. The converters are heated by burning producer gas around them, since the amount of heat developed in the reaction is slight. The hot gases go through heat exchangers, and are then scrubbed with water in order to get the hot-water supply for the saturators. The amount of carbon monoxide is reduced by this method to 3% or less. By compressing the cold gas to around one-thirtieth of its original volume, all but 0.1% or 0.2% of the carbon dioxide is taken out in water solution. A part (70%) of the energy used to compress the gases may be recovered by releasing the pressure upon the water solution of carbon dioxide. The gases are now further compressed to the pressure used in the synthesis, and the remainder of the carbon monoxide is taken out. The methods for getting rid of this component include absorption in ammoniacal cuprous solutions and passing the gases over a methanol catalyst. Other impurities may be removed by producing a small amount of ammonia and using it as a scrubbing liquid. (Where hydrogen from the electrolysis of water is sufficiently cheap,

the oxygen of the air may be removed by combining it with a portion of the hydrogen, leaving the proper mixture of nitrogen and hydrogen.) The final adjustment of proportions of nitrogen and hydrogen made by the water-gas process is obtained by adding small amounts of nitrogen from the liquid-air process.

2. Conversion. The mixture of nitrogen and hydrogen next passes into the converter in which the catalyst is contained. The converter is essentially a thick-walled tube or cylinder of varying construction and dimensions. In some cases there are several concentric cylinders, and there are usually provisions within the converters for heat exchange. The heat of reaction is not sufficient to bring the entering gases to the optimum temperature. Nichrome electrical resistors are commonly used to raise the temperature initially. Where very high pressures are employed and small-diameter converters are possible, the heating may be done by winding the outside of the converter with resistance wire.

The production of a satisfactory catalyst is a vital part of the process. Metallic iron of a spongy and porous nature is the main component of the catalyst mass. Iron alone will act as a catalyst, but is greatly assisted by other elements in small amounts. The most effective catalysts have been prepared by burning iron to magnetic oxide of iron in the presence of oxygen, fusing the oxide by electrical resistance on a bed of the same material, and adding the promoters, these being mainly potassium and aluminum.

The material of the converter is selected with a view to its resistance to the action of hot hydrogen under high pressure. Ordinary carbon steel is useless, since the hydrogen will remove carbon with the formation of methane, leaving practically soft iron. Alloy steels containing mainly chromium and tungsten with very small amounts of carbon and vanadium have proved successful, provided the shell itself is not heated above 300° C. Still safer are alloys containing 80% to 85% nickel and the remainder chromium. The catalyst tube is so designed that the entering gases, which are well below the temperature at which hydrogen is injurious to steel, come in contact with the walls of the tube. The higher temperatures during conversion are developed well away from the walls, the heat being taken up by these entering cooler gases.

The most commonly used pressure is 3000 lb. per square inch. Very few plants use pressures as low as 1500 lb.; some go to 15,000 lb. Naturally, with such high pressures the converter may be quite small, a typical one being 6 ft. long and 4 in. inside diameter. There are

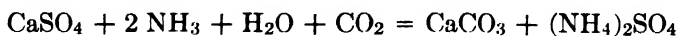
records of catalyst tubes in a process using 3000 lb. pressure which are of the order of 40 ft. in length, 3.5 ft. outside diameter, 1.5 ft. inside diameter, and up, of several concentric shells, with insulating layers, and a space between two of the shells for nitrogen at a pressure equal to that within the catalyst space.

In no process is all the nitrogen and hydrogen changed to ammonia, the amount being even less than the equilibrium value. The rate of flow in cubic feet per hour per cubic foot of catalyst space varies from 20,000 to 150,000, the percentage yields being less with higher velocities.

3. Ammonia Recovery. Ammonia may be recovered from the gases escaping from the converter by scrubbing them with water at the same high pressure. It is easy to liquefy the ammonia by cooling the gases, both water and boiling liquid ammonia being used as cooling agents. At very high pressures, liquefaction is particularly easy. In order to control the temperature in the converter more closely, part of the ammonia may be left in the gases that are recirculated. It is not feasible to continue recirculation indefinitely without removal of part of the residual gas because of the accumulation of argon and other inerts. At high pressures when there is 50% or higher conversion, the gases are not recirculated.

Products from Synthetic Ammonia. There is only a limited demand for anhydrous and aqua ammonia as a refrigerant. The production of hydrogen from ammonia makes possible the transportation of larger quantities of hydrogen than in the form of compressed hydrogen. The bulk of synthetic ammonia is used in the making of fertilizers, or is converted to oxides and oxygen acids of nitrogen. The common ammonium compounds made from synthetic ammonia are as follows.

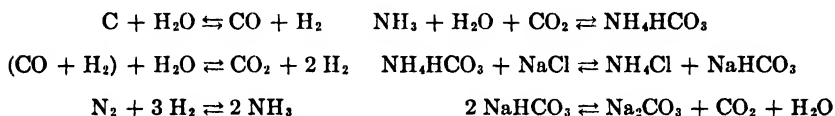
Ammonium Sulfate. Since carbon dioxide from the water-gas purification process is available in large quantities, and in Germany gypsum is both cheap and abundant, a method of making ammonium sulfate commonly employed in that country is the action of calcium sulfate on a solution of ammonium carbonate.



Ammonium sulfate is recovered by evaporation after the removal of the precipitated calcium carbonate. Where calcium sulfate is not available at a reasonable price, ammonium sulfate is made in the same way as in the by-product coke industry.

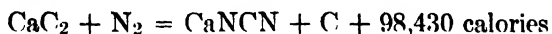
Ammonium Nitrate. Nitric acid is now largely made by the catalytic oxidation of ammonia and neutralized with more ammonia to produce ammonium nitrate. A widely used fertilizer material made by European fixation plants is known as "Leuna Saltpeter"; it is a double ammonium sulfate-nitrate in which about one-fourth of the nitrogen is in the nitrate form. A "shotted" mixture of ammonium nitrate and chalk is known as "nitrochalk."

Ammonium Chloride. A combination of processes produces both sodium carbonate and ammonium chloride. The limiting factor is the demand for ammonium chloride, which as yet is not very extensive. Large quantities of carbon dioxide are produced in connection with the preparation of nitrogen and hydrogen for ammonia manufacture. A summary of the reactions follows.



Ammonium phosphate and urea are also made and rather extensively used, but the demand for these compounds is as yet limited in comparison with that for ammonium sulfate and ammonium nitrate. Ammonium phosphate has the advantage of containing both nitrogen and phosphorus, which means considerable saving in transportation costs. For making ammonium phosphates, phosphoric acid from the electric-furnace process has an advantage over that from the sulfuric acid-calcium phosphate process, since it is stronger and requires less heat to dry the product. By means of an extrusion process, fused ammonium phosphates may be formed with small cylindrical granules, which are easily incorporated into mixed fertilizer. Where potash salts are produced near fixation plants, double potassium-ammonium nitrates are made. Urea is prepared in considerable quantities by the combination of carbon dioxide and ammonia, ammonium carbamate, $\text{NH}_2\text{COONH}_4$, being formed as an intermediate product. Most urea made by this process finds its use in Europe, but in 1929 the United States imported around 20,000 tons of urea and "calurea" for fertilizer purposes.

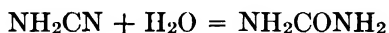
Calcium Cyanamide and Its Products. When calcium carbide is brought in contact with gaseous nitrogen at a high temperature, the nitrogen is readily absorbed, with the formation of calcium cyanamide and carbon.



Calcium cyanamide undergoes hydrolysis in the cold with the formation of an acid salt, which in turn may be hydrolyzed to free cyanamide.

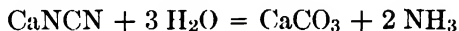


If a fairly high hydrogen ion concentration is maintained at temperatures not exceeding 10° C., urea is obtained.



Since large quantities of carbon dioxide are evolved in the calcination of limestone to produce quicklime for the cyanamide process, this gas may be used to liberate cyanamide from the crude calcium cyanamide. The free cyanamide may be treated with sulfuric acid, and, by adding calcium carbonate to neutralize the excess of free acid, the calcium is removed as calcium sulfate and a solution of urea is left behind. Some other valuable derivatives may be obtained from cyanamide, but the amount produced is small, and the materials may be classed under the head of fine chemicals.

When calcium cyanamide is treated with a hot, dilute, caustic soda solution, complete hydrolysis takes place.



The ammonia is not allowed to escape until fairly high pressures are developed in order that the temperature of hydrolysis may be as high as possible. Although the cyanamide process may be used to make ammonia, this process is uneconomic in comparison with the direct synthesis of ammonia. A most important reaction of calcium cyanamide is its fusion with salt to produce a crude cyanide. It will be noted that the carbon necessary is already present in crude cyanamide.



Salt is regarded as a flux. Commercially pure sodium cyanide may be obtained from this material, and it is also used as a source of hydrogen cyanide. Industrial cyanides are largely produced by this process, thousands of tons being used annually.

The Muscle Shoals Cyanamide Plant. During the World War the United States built an enormous calcium cyanamide plant at Muscle Shoals, on the Tennessee River, in order to manufacture ammonium nitrate. The plant was built in a remarkably short time and was

found satisfactory on test runs, but it was never operated regularly, and it is now in "stand by" condition. The economic and political questions which this plant has raised are discussed in an earlier chapter. This plant represents quite well the method of operation of the cyanamide process, and thus will be described in some detail.

Coke and quicklime were fed into combination arc and resistance furnaces, and from these molten calcium carbide was tapped. The chilled carbide was crushed and ground to 200 mesh in an atmosphere of nitrogen. This precaution was necessary since moisture of the air produces acetylene, which forms explosive mixtures with air. The powdered carbide to the amount of 1500 lb. was charged into vertical cylinders equipped for introduction and removal of gases. The cylinder served as one electrode, and a long pencil of graphite reaching down into the charge was the other. Nitrogen was admitted to the bottom of the furnace. A current of 100 volts and 250 amperes was passed for 20 minutes, and a smaller current for several hours longer. When the temperature reached $1000^{\circ}\text{C}.$, the current was cut off and the reaction maintained itself. Nitrogen was continually introduced until all the carbide was converted to crude calcium cyanamide, the total time required being of the order of 40 hours. The final temperature attained was around $1100^{\circ}\text{C}.$ The reaction products after cooling were in the form of a solidly sintered cake. The product had this average composition:

Calcium cyanamide	61.2%
Calcium oxide	20.0%
Carbon	13.5%
Calcium carbide	1.5%

The remainder includes the ash of the coke and impurities in the lime.

In order to prepare ammonia from crude calcium cyanamide the material was finely ground in an atmosphere of nitrogen and given a preliminary treatment with small amounts of water. This served to decompose the unchanged carbide with the evolution of acetylene, and to slake the quicklime present. The treated material was then placed in autoclaves along with a 3% solution of sodium carbonate. Air was passed through to remove acetylene and phosphine, which are catalyst poisons in the subsequent catalytic oxidation of the ammonia. The resulting caustic soda solution brought about complete hydrolysis of calcium cyanamide when steam under pressure was admitted to the autoclave. At 250 lb. pressure, steam and ammonia were allowed to escape at a sufficient rate to maintain a constant pressure. Towards

the end of the operation the pressure dropped to atmospheric. More steam was put in, and the operation was repeated until the amount of ammonia coming off was too small to make further treatment profitable. Entrained solids were removed by a system of baffle plates, and steam was condensed. The contents of the autoclave were filtered, and the calcium carbonate sludge was discarded. The filtrate was used in the scrubbing towers of the nitrogen plant to remove carbon dioxide from the air, and this was used again in the autoclaves. The plant at Muscle Shoals used 7 rotary lime kilns each 125 ft. long; 12 carbide furnaces, each with a capacity of 60 tons; a 300-ton capacity nitrogen plant using the liquid-air process; 1536 nitrifying ovens, which would hold 1 ton each; 56 autoclaves, each 6 ft. in diameter and 21 ft. long and handling 4 tons of carbide; 696 catalyzer units; and 24 towers for nitrogen oxide absorption, each tower being about 1000 sq. ft. in cross-sectional area and 60 ft. high.

The large plant producing calcium cyanamide and its derivatives at Niagara Falls, Ontario, has been modernized in recent years, and now has an annual capacity of 75,000 tons of fixed nitrogen, which means around 355,000 tons of the crude calcium cyanamide. Originally, 20,000 kw.-hr. were required per ton of nitrogen fixed, but this has been successively reduced to 9000 kw.-hr. In the same way, the requirements per ton of nitrogen have been reduced for limestone from 7.5 to 4.8 tons and for coke from 3 to 2 tons. The lime-nitrogen furnaces use a charge of 8000 lb. of finely ground calcium carbide. In general, however, the process is the same as that described above, differing in being greatly improved in many important details that are beyond the scope of this discussion.

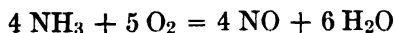
Oxides of Nitrogen. The two most important oxides of nitrogen are nitric oxide, NO, and nitrogen dioxide, NO₂. Nitric oxide reacts readily with oxygen of the air to form nitrogen dioxide at temperatures below 700° C., and at room temperature oxidation is quantitative. Nitric oxide is thus the only oxide that is manufactured directly, all other nitrogen oxides and their derivatives being made from it. There are two commercial methods for making nitric oxide: direct synthesis from the nitrogen and oxygen of air, and catalytic oxidation of ammonia. The former process, generally known as the "arc process," is rapidly becoming obsolete. Even where hydroelectric power is very cheap, the direct synthesis of ammonia is taking its place. Since the arc process was the first successful method of fixation of nitrogen, it possesses sufficient historical interest to be described somewhat out of proportion to the present importance of the method.

Arc Processes. A study of the nitrogen-oxygen equilibrium, $\text{N}_2 + \text{O}_2 + 43,200 \text{ calories} \rightleftharpoons 2 \text{ NO}$, indicates that the formation of nitric oxide is favored by the application of heat. Unfortunately a temperature attainable commercially only by the use of the electric arc is required before appreciable velocities and yields are realized. Less than 3% of the total energy employed is taken up in the reaction. Above 2300°C . the time required to reach equilibrium is so short as to justify the reaction as being considered instantaneous. The higher the temperature, the greater are the yields. The reaction mixture must be cooled as quickly as possible after it passes through the electric arc, but the decomposition below 1200°C . is so extremely slow that nitric oxide may be regarded as a stable compound below that temperature. In spite of every effort to cool rapidly, rarely more than 2% and usually not more than 1.2% of the mixture is nitric oxide by the time 700°C . is reached. Below this temperature, oxygen begins to react with nitric oxide to form the dioxide, thereby giving a double insurance against decomposition of the original product. ($2 \text{ NO} + \text{O}_2 \rightleftharpoons 2 \text{ NO}_2 + 27,800 \text{ calories}$.) The various processes differ in the way in which the air is preheated, the arc spread, and the gases cooled.

In the Birkeland-Eyde process the arc was spread by means of a magnetic field. The ends of the electrode were between the poles of a powerful electromagnet, and the arc assumed the form of a half disk of flame. Since the current that passed between the electrodes was alternating, the half disk was alternately above and below the electrodes. The reaction chamber within a massive cylinder of granite and firebrick was circular in cross section and quite thin, the dimensions being of the order of 6 ft. in diameter and 3 in. in thickness. The Schoenherr furnace utilized an air blast to spread the arc, a whirling motion being imparted to the air by admitting it tangentially. The Pauling furnace also used an air blast, the arc being spread into a fan-shaped flame.

With the exception of an ill-fated early venture at Niagara Falls and a small plant which operated for a few years in the Pacific Northwest and made sodium nitrite, the arc process was never used in the United States. No new plants are being built anywhere, and the production of existing plants represents only a very small fraction of the total fixed nitrogen of the world.

Ammonia Oxidation. Ammonia from any source may be catalytically oxidized to nitric oxide, the reaction being



Although theoretically pressure drives this equilibrium to the left, many plants operate under pressures of the order of 100 lb. to the square inch. Pressure favors the later absorption reactions, and the size of the plant is much smaller. It is necessary that the ammonia be relatively free from catalyst poisons. It is common practice to employ air as a source of oxygen, with ten volumes of air per volume of ammonia. Platinum is most commonly used as a catalyst and is sometimes alloyed with smaller amounts of iridium or rhodium. The gauze is usually 0.003 in., woven 80 meshes per linear inch. The gauze may form a partition between two sections of an aluminum box, but is more commonly rolled into a cylinder of four thicknesses, which is supported by a nickel sleeve and closed at the opposite end by a silica disk. A circular gauze 13 in. by 114 in. will form a cylinder 9 in. in diameter. Ammonia is not preheated because of ease of decomposition into nitrogen and hydrogen, and is not mixed with the preheated air until it reaches the converter. Up to 1500° C. the equilibrium mixture represents 99% conversion, and even at 1000° C. the reaction is sufficiently rapid to give 85% to 95% yields with relatively high speed of gases. After a period of use the platinum surface becomes roughened and is more effective than fresh wire. Base-metal catalysts have never proved as effective as platinum, but some progress has been made in their use, particularly where oxygen is substituted for air. The products of oxidation are sent through heat exchangers to preheat the air used for combustion and are handled largely in chromium-iron apparatus.

Nitric Acid. Nitric acid in pure form is colorless, but commercial grades are colored by the presence of dissolved oxides. The anhydride of nitric acid, nitrogen pentoxide, N_2O_5 , is not stable at ordinary temperatures, but the NO_2 - N_2O_4 equilibrium mixture is soluble up to 12% in nitric acid. Nitric acid and water form a constant-boiling mixture at 760 mm. pressure of 68% nitric acid and 32% water with a boiling point of 110° C. The commercial grades commonly quoted are:

36° (1.530)	52.3%
38° (1.355)	56.5%
40° (1.381)	61.4%
42° (1.408)	67.2%

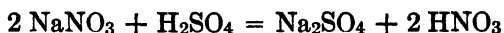
The first and last are the ones most commonly used. It is possible to produce 99% nitric acid; but since oleum is used in making mixed acid, material as weak as 88% can be used. The common uses for nitric acid are: nitration of glycerin, cellulose, and aromatic hydro-

carbons as a part of processes resulting in explosives, plastics, lacquers, dyes, and pharmaceuticals; in metallurgical operations such as parting gold and silver; the pickling of brass; photoengraving; and production of nitrates, among which are copper, silver, sodium, and ammonium. Badger states that the distribution of nitric acid is as follows:

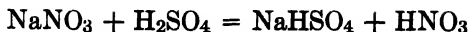
Explosives	75%
Pyroxylin plastics	10%
Chemicals and dyes	8%
Nitrocellulose lacquers	5%
All other uses	2%

Until recent years, nitric acid was made almost entirely by mixing sodium nitrate and sulfuric acid and distilling the more volatile nitric acid from the mixture. Comparatively little nitric acid finds its way into chemical industry from arc-process nitric oxide, but this substance made by ammonia oxidation is continually increasing in importance as a source of nitric acid. Nitric oxide has now largely supplanted nitric acid from "niter potting" as a source of make-up catalyst in the lead chamber process for sulfuric acid. The two main products of the arc process are calcium nitrate and sodium nitrite. Nitric acid is a difficult material to handle, and practically all large users of this acid manufacture their own where it is to be used. Mixed acid, which is a mixture of sulfuric and nitric acids, can be shipped in steel tank cars, but most nitric acid is shipped in glass carboys.

Sodium Nitrate Process. The standard process by which nitric acid is made from sodium nitrate and sulfuric acid consists in charging coarsely powdered sodium nitrate into an iron pot still with a conical bottom to facilitate discharge of the molten residue, and adding the desired amount of sulfuric acid. The still, suspended in a brick setting, is heated by gases from a firebox, which is set to one side to prevent direct flame from impinging upon the still. The gases pass over the entire surface of the still including the top. A typical run produces around 2½ tons of acid of average strength of 87% in 12 hours' time. The strength runs up rapidly until at the end of the first hour a 99% acid is coming off. Towards the end of the run, water is driven out of sodium hydrogen sulfate with the formation of sodium pyrosulfate. If strong acid is required, several receivers are used to collect material of different strengths. The amount of sulfuric acid used is greater than that theoretically necessary for the equation



and is either somewhat less or slightly more than that required by the equation



The melting point of sodium sulfate is about 800° C., which is a bright red heat. It is not commercially feasible to heat the residue to such a temperature and run the molten mass from the still, nor desirable to allow the residue to cool in position and dig it out as a solid. Sodium hydrogen sulfate melts at 300° C., but the eutectic of these two salts, which is approximately 5 NaHSO₄ · 3 Na₂SO₄, melts at 188° C. Sulfuric acid is either used in such amounts that the eutectic is approximately attained, or enough acid is used to form the acid sulfate alone with some free acid. This residue is known as "niter cake." Some plants making nitric acid by this process run the niter cake while still molten into furnaces along with salt and make hydrochloric acid. The sulfuric acid used in the manufacture of nitric acid must contain 7% to 8% water to avoid decomposition of the nitric acid and excessive formation of oxides of nitrogen. The sodium nitrate should not contain more than 2% of sodium chloride. Most of the hydrogen chloride produced by the action of sulfuric acid escapes, but causes some loss of nitric acid by this reaction.

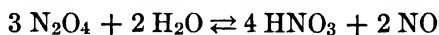
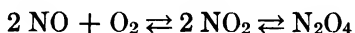


At a certain stage of the distillation the reaction mixture sets to a porous solid which soon melts. This constitutes the chief difficulty of continuous processes and makes stirring in a vacuum process difficult.

The vapors from the pot still are conducted down through a sloping iron pipe, in which there is some condensation, into a receiver. The receiver is equipped with a return condenser, made up of S bends of silicon-iron, or fused silica, or of glass tubes set into vertical headers. Cooling is so regulated with water sprays that the acid runs back into the receiver near its boiling point. The oxides of nitrogen are not soluble in nitric acid at this temperature, and hence are carried on. Those which escape conversion in the cooler parts of the condensers pass to oxidation and absorption units. In the usual process, from 10% to 20% of the nitric acid formed in the reaction between sodium nitrate and sulfuric acid is decomposed in the still, and the oxides formed must be recovered, partly during condensation, and partly in a series of recovery towers.

Oxide Absorption Processes. Nitric acid results from the combined oxidation of nitric oxide to nitrogen dioxide and its absorption in

water. This applies to any process which makes nitric oxide. Although the design of the equipment varies according to the concentration of the nitric oxide in the gases, the principle in all cases is the same. The arc process gives a gas containing not more than 2% nitric acid. The catalytic oxidation of ammonia results in a gas of the order of 15% nitric oxide. The gases from the sodium nitrate process of nitric acid manufacture are quite rich. The reactions are somewhat complicated, but they may be satisfactorily represented thus:



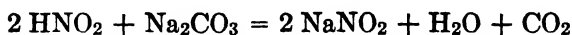
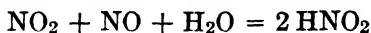
There is probably intermediate formation of nitrogen trioxide, which with water gives nitrous acid. This in turn decomposes into nitric acid and nitric oxide.

Only a part of the oxides are absorbed, and oxidation must go along with absorption. The counter-current principle is used in this process, the most dilute acid meeting the gas containing the least nitrogen oxides. It is impossible to produce an acid stronger than that represented by the minimum vapor pressure of the two-component system at the temperature of absorption. In practice, this concentration is never reached, a common value being of the order of 61%. With a gas containing originally very little nitric oxide, a condition characterizing arc-process gas, it is not possible to recover more than 80% of the fixed nitrogen as nitric acid. Most of the remainder may be obtained as sodium nitrite by passing the gas through a solution of sodium carbonate. When the gas is richer in nitric oxide, absorption is more nearly complete, and no system of final recovery by alkaline solution is necessary.

The older towers were made of granite, and those used with the arc-process gas were of enormous size. In modern plants making nitric acid from nitric oxide produced by ammonia oxidation, relatively small towers* of chromium steel are used and absorption is carried out with the gases under pressure of 100 lb. per square inch. The absorbing acid is circulated, cooled before returning to each tower, and progressively moved counter current to the gas stream until the maximum strength consistent with economic operation is obtained. When pressure absorption is used, the spent gases may serve to supply part of the power necessary to compress the air for catalytic ammonia oxidation.

Concentration of Nitric Acid. The concentration of acid from modern absorption towers is of the order of 60%. Beyond that point, concentration is brought about by adding concentrated sulfuric acid and heating the mixture. Oleum is still more effective, the sulfur trioxide present combining with the water. Sulfuric acid forms stable hydrates with water and permits the escape of relatively concentrated nitric acid. The best method of heating the mixture is to run steam into it. The amount of water vapor from sulfuric acid-water mixtures is quite low, even up to fairly high water content. With 30% water in the mixed liquids a 90% nitric acid may be obtained. Although 99% nitric acid has been obtained by this method, it is rare that higher than 95% needs to be reached. The mixture of sulfuric acid, nitric acid, and water flows down a tower or fractionating column, while steam is introduced at the base of the tower or column. The vapors issuing from the top pass through condensers, and the receivers are protected by oxide absorption towers. This same method is employed in the recovery of nitric acid from mixed acid that has been used until it contains too much water and too little nitric acid to be profitably "fortified" by oleum.

Nitric Acid Derivatives. The dilute nitric acid obtained from the towers of the arc process is converted into a crude *calcium nitrate* by the action of nitric acid on limestone. This is used directly as a fertilizer material, but has the disadvantage of being markedly hygroscopic. The production of *ammonium nitrate* is particularly convenient in connection with ammonia oxidation processes. A portion of the ammonia is converted into nitric acid, and the remainder is bubbled through the dilute acid in tanks and towers. The solution of ammonium nitrate is evaporated until only molten salt remains. The melt is allowed to cool, and by proper regulation of cooling and stirring, fine crystals are formed, a process known as "graining." *Sodium nitrate* is now being made extensively by treating sodium carbonate with nitric acid made by the ammonia oxidation method. In some of the large German synthetic ammonia plants, the sodium carbonate is made from salt, from the waste carbon dioxide of the water-gas process for hydrogen, and from the ammonia, with the simultaneous production of ammonium chloride. *Sodium nitrite* is obtained by scrubbing the gases containing oxides of nitrogen with sodium carbonate, the reactions being most simply represented as follows:



Sodium nitrite is a necessary reagent in the manufacture of a considerable number of important synthetic organic dyes, and is also used to some extent in meat packing.

Chilean Sodium Nitrate. In the Atacama Desert in Chile, a strip of land some four hundred miles long and never more than a few miles wide, lying along the 70th meridian and at an elevation of 3000 to 7000 ft., contains extensive deposits of sodium nitrate. These deposits are not continuous, but are massed in certain spots, which are, however, reasonably well distributed over the area. Sea fogs and dews bring some moisture to this region, but there is practically no rainfall. There has never been an adequate survey of these deposits. It is probable that the richest of them have been worked, but any estimate of the remaining nitrate without thorough exploration is little better than a worthless guess. Sodium nitrate was for many years the largest single source of revenue of the Chilean nation, since an export tax of about \$12 per ton was levied on this material. In 1930 the whole system was changed with the formation of a corporation known as "Cosach" (an abbreviation of a title which means Chile Nitrate Company), in which the Chilean government and practically all nitrate producers joined, the government holding one-half of the stock. Undeveloped land to the extent of 150,000,000 acres was turned over to the producers. The export tax was repealed, and instead the corporation guaranteed the Chilean government a fixed income beginning at \$22,000,000, to be progressively reduced to a level of \$17,000,000 in 1933. After that time the state was to share the income from the stock. The whole scheme was a dismal failure, and the industry is in a highly unsettled state.

The deposits are overlaid with sodium sulfate and with silicates. Sodium nitrate occurs in what is known as "caliche" along with sodium chloride and insoluble materials. Badger gives the following as the typical upper and lower limits of caliche: *

Sodium nitrate	14-30%
Potassium nitrate	2- 6%
Sodium chloride	2-25%
Calcium sulfate	2- 6%
Sodium and magnesium sulfates	2- 6%
Sodium iodate	0.02-0.2%
Sodium and calcium borates, perchlorates, chromates, sulfonitrates, vanadates	Traces
Insolubles	25-59%

Deposits much lower in sodium nitrate than 14% are now being suc-

* Tabulation quoted from Badger and Baker's "Inorganic Chemical Technology" by permission of The McGraw-Hill Book Co.

cessfully worked, the caliche running between 8% and 10% sodium nitrate. Little effort is made to separate potassium from sodium salts. Most of the iodine present is wasted, since the amount used in the chemical industry is small.

The modern method of producing sodium nitrate used by the more important refineries is based on sound principles of physical chemistry. In it the fines are screened from the run-of-mine, and the lump material is broken to $\frac{3}{8}$ -in. size. This is screened, and the fines from this and the first screening are mixed with mother liquor and the suspension filtered by open tank dipping leaf filters. The lump material is leached in tanks through which liquids are circulated counter current. Heat is furnished by Diesel engine exhaust gases, extraction being carried out at about 40° C. The warm concentrated solutions are cooled, first by cold depleted liquor from the crystallization operations. These mother liquors are sent through ammonia condensers as the cooling liquid and are thus warmed up and returned to the extraction tanks. The saturated solution is further cooled in shell and tube ammonia refrigerators. The crystals that separate are removed by means of Dorr thickeners, and this sludge is freed of adhering liquid in centrifugals. The product at this stage is in the form of very fine crystals, which take up water and set to hard masses. In order to obtain a material that will not form lumps, that will flow, and that can be mixed with other materials, the crystals are briquetted, the briquettes are melted, and the molten material is sprayed, thus cooling in tiny pellets with a hard surface glaze, which do not readily take up water.

Power Consumption in Synthetic Fixation Processes. The bulk of the power used in the two older processes for nitrogen fixation was electrical, and this constituted the chief cost. In the direct synthesis of ammonia, the power factor is small unless hydrogen is derived from electrolysis of water. The cost varies in this case depending on whether or not nitrogen is obtained from liquid air or by the removal of oxygen from air by burning it with hydrogen. The following table of costs is generally accepted as correct in the nitrogen fixation industry.

PROCESS	KILOWATT HOURS PER METRIC TON NITROGEN
Arc	68,000
Cyanamide	9,000-15,000
Synthetic ammonia:	
(Hydrogen from water gas)	2,500- 4,000
(Hydrogen by electrolysis)	14,000-20,000

Fixed Nitrogen Production. The rate of production of fixed nitrogen by the three processes outlined in this chapter has increased very rapidly since 1924. From 1910 to 1916, the curve of production had a very sharp upward slope, but for the next eight years showed some decline. In terms of thousands of metric tons of nitrogen, the total was around 400 in 1924 and had reached 1200 in 1929. The curve of synthetic ammonia practically parallels the curve of total production. The arc-process curve is now practically flat at 16 with a slight decline, and the cyanamide curve after a slump after 1917 about regained its former position of around 240. Synthetic ammonia processes in 1929 showed a value of 900.

Fixed nitrogen from all sources in 1928-1929 had the following distribution:

MATERIALS	1000 METRIC TONS NITROGEN
Chilean nitrate	540
Ammonium sulfate from synthetic ammonia	535
Ammonium sulfate from by-product coke ovens	414
Other synthetic nitrogen compounds (mainly anhydrous and aqua ammonia)	402
Calcium cyanamide	231
Calcium nitrate	150
By-product aqua ammonia	56

CHAPTER XIII

SILICATE INDUSTRIES

In general, the two terms "silicate industries" and "ceramic industries" are synonymous. The word "ceramics" is derived directly from the Greek word for "potter," which in turn comes from the Sanskrit verb meaning "to burn." Hence ceramic materials may be regarded as "burnt stuff" produced from earthy substances by the application of heat. Hewitt Wilson in his book, "Clay Technology," gives these three groups of ceramic products.

1. Products whose main component is clay, that are molded in a wet and plastic condition, dried, and burned at a high temperature, and that derive their strength from the partial fusion (vitrification) of silicates. Structural, abrasive, refractory, and insulating materials fall in this classification. Vitreous enamels and glazes may also be included, although in these cases fusion is more nearly complete.

2. Products that are heated until they become fluid, and are molded in a viscous liquid state and carefully cooled to avoid strains. Glass and fused silica are the chief products in this class.

3. Pulverized products made by heating raw materials to a high temperature in order to convert them into substances having cementing properties. Lime, plasters, and cements are included in this group.

Since this book is written on the basis of a chemical classification, both lime and gypsum are discussed in the chapter on Sodium, Calcium, and Magnesium Compounds. The emphasis in this chapter is laid on silica and silicates.

For centuries, all progress in the ceramic industries was made by trial and error methods. Glass and pottery were ancient arts, which had reached a high degree of perfection. Until very recently, portland cement was made on the basis of formulas that repeated trials had proved to be satisfactory. It has been pointed out, however, that the glasses of ancient and medieval times were quite inferior to modern glasses both from the standpoint of chemical composition and freedom from defects.

All modern developments in these industries are based on thorough

and fundamental equilibrium studies of the one-component system of silica alone, two-component systems of silica and a series of oxides, and three-component systems, among which the two most important are silica-lime-soda, and silica-lime-alumina. Colloid chemistry plays a most important part in all ceramic industries.

GLASS

The term "glass" is applied to non-crystalline products of fusion. Although what is known in industry as "glass" is hard and has considerable mechanical strength, it may be regarded as a supercooled liquid. Since "vitrification" refers to incipient fusion of a mixture of granular solids, "devitrification" refers to the formation of crystals from a material in the vitreous or glass state. Individual silicates differ greatly in the readiness with which they devitrify, or pass from the vitreous to the crystalline state. Pure sodium metasilicate, $\text{Na}_2\text{O} \cdot \text{SiO}_2$, crystallizes very readily, and it is practically impossible to undercool the molten material. The silicate having the formula $\text{Na}_2\text{O} \cdot 3 \text{CaO} \cdot 6 \text{SiO}_2$ is very easily supercooled and is a viscous and readily workable material at temperatures above its freezing point. Hence most commercial glasses are within the region with respect to their soda-lime-silica content represented by this compound. The matter is further complicated by the presence of such substances as alumina, which lower the melting point still further. The enormous lowering of the melting point of a simple substance by the addition of another is strikingly illustrated by the fact that the addition of 25% of sodium oxide to silica changes the melting point from 1710°C . to 793°C . Those compounds which devitrify readily are obviously unsuited for industrial glass manufacture, since the glass products must be formed and cooled without devitrification, and must remain practically free from this tendency for a long period of time while they are in use.

Industrial glass is essentially a complex solution of compounds, and is like any other mixture of molten salts in that very definite equilibrium relationships obtain. It differs solely in that it is very easy to cool it below its melting point to an undercooled condition, which is practically permanent. Owing to this property it is extremely difficult to determine its melting point by simple methods. This property also makes it industrially valuable.

Other properties that give glass industrial value are: transparency, smoothness, hardness, refractive power, and resistance to solution and

chemical action. Not all glass is transparent, but most glass is at least translucent. A particular form of chemical action that is important is "weathering," or the combined action of water and the gases of the atmosphere on glasses that are continually exposed. The viscosity of the molten material is important in fabrication, particularly with reference to the ease with which bubbles escape, and in gathering and forming. It is also necessary to know the range of temperature between easy flow and setting.

The various physical properties of glass, such as specific gravity, tensile strength, compressive strength, hardness, coefficient of expansion, specific heat, heat conductivity, resistance to elastic change, devitrification range, refractive power, and dispersive power, may be varied within fairly broad limits by altering the amounts of the materials from which the glass is made. The coefficient of expansion is of considerable importance if the glass is to be subjected to sudden changes of temperature, as for example baking ware and chemical laboratory and chemical plant equipment. Using the linear coefficient of expansion multiplied by ten million to get whole numbers, the values of different silicate materials may be compared.

MATERIAL	$\alpha \times 10^7$
Fused silica	5.4
"Pyrex" brand chemical glass	32
Porcelain (average)	40
Jena glass	50
Ordinary glass	85-125

Invar, an alloy of 64% iron and 36% nickel, has on the same scale a value of 9. Most metals, however, have much higher coefficients of expansion, these being of the order of 100 to 300.

Many substances are used in the glass industry, but the bulk of commercial glass may be regarded as made up of three components: silica, SiO_2 ; lime, CaO ; and soda, Na_2O . It is entirely beyond the scope of this book to discuss the phase relations even in the silica-lime-soda system. An excellent discussion of this subject may be found in the *Journal of Chemical Education*, 8(1931), 420-441, entitled "Glass, Its Composition and Properties," by George W. Morey of the Geophysical Laboratory, Carnegie Institution of Washington.

Raw Materials. The common raw materials used in making glass are as follows.

Silica, SiO_2 . Very few glasses are made without silica, and in most glasses it is the main ingredient of the batch. It is used in the form of quartz sand that is practically pure silica. Iron produces color in

glass. Cheap bottles and those glasses that are intentionally colored can be made from sand in which there is an appreciable amount of iron oxide. Plate glass may tolerate as much as 0.07%, but the amount permitted in most colorless glass is less than this value, and in optical glass should not be over 0.02%. Iron may be partially removed by the use of electromagnetic separators for the free metal and magnetic oxide, and hydrochloric acid for all the oxides. The size and shape of the sand grains are important as well as the amount of impurities, everything but silica being regarded as impurities.

Lime, CaO. This component is introduced as the oxide, hydroxide, and carbonate. Dolomite is also used, which includes magnesia, a desirable component in certain glasses.

Soda, Na₂O. Soda greatly lowers the melting point of silicates. It is introduced as soda ash, Na₂CO₃, and salt cake, Na₂SO₄. Salt cake is used mainly to get rid of scum in glass tanks, but it is said to attack refractories to a greater extent than soda. Sodium sulfate must be reduced by carbon to sodium sulfite in order to make possible the formation of silicates.

In addition the following substances find use in transparent and uncolored glasses.

Magnesia. A limited amount of magnesia increases the stability of glass and lowers the tendency to vitrify. It is rarely substituted entirely for lime, but for some purposes its use along with lime is quite beneficial.

Lead Oxides. Litharge, PbO, and Red Lead, Pb₃O₄. Lead in glass increases the refractivity and dispersivity, and therefore is used in optical glass and cut glass. It is used also in electrical tubing, but has been displaced by lime in making electric light bulbs.

Potash, K₂O. Potash changes the viscosity curve of glass and prevents devitrification. Its use is limited to lead glasses and to those glasses which are exposed to the weather. Potash glass is probably no more resistant to weathering than soda glass, but the carbonate is hygroscopic and does not give a cloudy appearance. This ingredient is introduced as potassium carbonate.

Zinc Oxide, ZnO. This component is in some of the heat-resisting glasses.

Alumina, Al₂O₃. In optical glass, alumina is introduced as precipitated aluminum hydroxide, but is more commonly put in as feldspar. Its main purpose is to lower the melting point and retard devitrification; it is a very common component of many varieties of glass.

Boron Compounds. Boric acid, H_3BO_3 , and sodium baborate, $\text{Na}_2\text{B}_4\text{O}_7$, are the boron compounds commonly used. They serve to decrease the coefficient of expansion and thus to give greater thermal endurance. Borosilicate glasses have wide use as insulators, chemical pipe lines, oven ware, and railway signal glass.

Oxidizing agents include sodium nitrate and potassium nitrate. Arsenic trioxide serves to remove bubbles. Ammonium nitrate was once used as a "fining" agent, but is now of little importance.

Color may be developed in glass in two ways. Colored compounds may be formed, or colloidal particles of the correct size may be produced and held in suspension to give color. If impurities such as iron have developed a slight color, this color may be neutralized by a coloring agent giving a complementary color. Among those substances which produce colored compounds, the following are most generally used.

Manganese Dioxide, MnO_2 . A mild pink is developed by small amounts of manganese to counteract the green of iron.

Iron Oxide, Fe_2O_3 . Iron compounds produce green to yellow shades, and are rarely added intentionally, but are regarded as impurities that are tolerated only in cheaper grades of glass.

Cobalt Oxide, CoO . It requires only very small amounts of cobalt to produce an intense blue. In order to regulate the shade, a very dark blue glass is made, and portions of this in powdered form are added to the batch of ingredients.

Uranium, Nickel, and Chromium salts are also used to a slight extent. The color produced by the above compounds is not affected by working conditions, but depends entirely on chemical composition.

Colloidal coloring agents are sulfur, carbon, selenium, copper, and gold. The true color does not develop at once, the molten glass being either colorless or a different color from the final one. The desired color can be obtained by regulating the heat treatment so that the dissolved or colloiddally dispersed coloring material separates upon nuclei formed in the colorless glass. It is necessary to have enough nuclei so that all the coloring matter is deposited to produce particles small enough to secure the correct color without turbidity. It is generally necessary to add the element that is to cause the color in the form of a compound along with a reducing agent that acts at the high temperature of the furnace to free the element. Selenium is added in the form of sodium selenite, Na_2SeO_3 , with a reducing agent, and is the most widely used of colloidal coloring agents. It gives a very high transmitting red glass. Selenium is used more than manganese dioxide

as a corrective, owing to the greater ease of color control. Copper is obtained by reduction of copper compounds, but gold compounds decompose readily in molten glass to give the metal without the use of a reducing agent. Sulfur must not be used in lead glasses. For certain purposes the color must be spectroscopically tested, and very pure colors have been developed which cannot be confused. This is particularly important in connection with signal lights. Various degrees of intensity of color may be obtained by "flashing," which means superimposing a thin layer of colored glass above a thicker layer of colorless glass.

Diffusing effects may be obtained by etching the surface with hydrofluoric acid or acid fluorides, and by the use of a sand blast. Opaque glass is made by adding such substances as fluorspar, cryolite, calcium phosphate, and stannic oxide to the batch before melting. These substances remain in colloidal suspension under the proper conditions. Opalescence may be obtained by the substances mentioned, and also by partial devitrification and separation of solid silica. Designs are etched on glass by protecting certain portions with wax or paraffin, and treating with hydrofluoric solutions or vapors.

Once the proper composition of a batch of glass has been determined, the remaining operations are mechanical in their nature, and consist of grinding and mixing ingredients, melting, removing the glass, working, and annealing.

Melting. The thoroughly mixed ingredients of a glass are melted either in pots or in tanks. The pots are deep clay crucibles, either open or covered, and with an opening on the side near the top. The pots, made of a very special grade of clay, are set in a circle in firebrick under a common stack. The hot gases impinge upon a refractory arch in the form of a shallow dome, which serves to reflect radiant heat on the pots. When a new pot is put in a furnace, it is previously brought up gradually to the proper temperature in a small auxiliary furnace called a "pot arch."

Tanks are most commonly arranged for continuous operation, although some are intermittently used, and are known as "day tanks." A glass tank is a shallow, rectangular vessel, made of fireclay or mullite blocks, above which is an arching fireclay roof, the whole functioning as a reverberatory furnace. The blocks are bonded by glass, which penetrates the spaces between them to a distance of one or two inches and solidifies. There is a charging hole at one end and one or more holes from which molten glass may be withdrawn. Special collecting hearths are provided for automatic gathering machines, and

other tanks are equipped with devices for continuous flow of a thin layer of molten glass to the equipment in which it is worked. The tank is divided into two sections by a permanent wall. The opening connecting the two sections is below the level of the molten glass. In this way, bubbles are prevented from reaching the discharge or working end of the tank.

Both tank and pot furnaces are heated by fuel gas, either natural gas or producer gas, or by fuel oil. Both regenerative and recu-

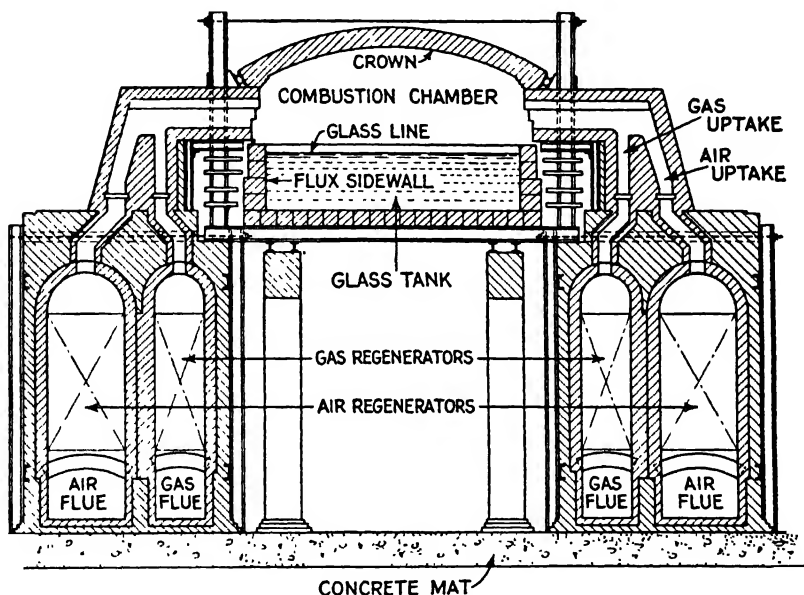


FIG. 69.—Glass Tank Courtesy Corning Glass Works, Corning, N. Y.

perative methods of preheating air and gas are employed in the glass industry, the former being more common. The temperatures attained are from 2500° F. to 2650° F. in glass tanks. Indicating and recording pyrometers with platinum, platinum-rhodium couples are commonly used, and are supplemented to some extent by optical pyrometers.

The action of molten glass on refractories is both physical and chemical. Mullite, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, as a material of construction for glass tanks represents a great step forward in this industry over the fireclay refractories once used exclusively. By means of this material many problems of refractories have been solved. Mullite is made by fusion in the electric furnace, cooling the molten material to a crystal-

line solid, grinding, molding into bricks or blocks, and reburning to vitrification.

Cracked, broken, and imperfect articles and trimmings, are all crushed together to a coarse powder called "cullet." Rarely less than 10% and sometimes as much as 80% of the charge of a pot or tank is cullet.

During the melting operation a great deal of gas is evolved, which serves to stir the charge. The contents of a pot are often stirred with fireclay rods or water-cooled iron pipes to obtain homogeneity, but tank furnaces are operated without the use of mechanical stirrers. Only about 10% of the fuel used goes to melt the raw materials. Considerable heat is used to keep the contents molten over long periods of time, and the radiation losses from the tanks and pots are large. This is excusable because of the difficulty of insulating the high-temperature surfaces of the furnaces without risking failure of the refractory materials.

Removal from Furnace. Glass is removed from the pot or tank in which melting takes place by one of the following methods.

1. *"Gathering"* either on a long iron tube known as a "blow iron" for making hollow ware, or on a "punty iron," an iron rod with a clay ball on the end dipped into the glass, for delivering a lump or "gob" to press molds. Large gathers are built up by successively dipping the gathering iron into the glass, cooling it slightly, and dipping it again for more glass. In some cases two or more kinds of glass are gathered, as illustrated by the flashing operation previously referred to. When a milk glass strip is necessary in thermometers and burettes, the opaque material is spread on one side of the gather of the original glass, and the whole is covered by clear glass.

2. *Ladling.* This is ordinarily for the purposes of rolling and pressing, but this method of removal may be used with other processes.

3. *Pouring* from an open pot, which has been lifted from its setting. This method finds use in the manufacture of plate glass.

These three methods are commonly used with pot furnaces. The following methods are used with glass tanks to supply glass-working machines.

4. *Vacuum gathering.* The glass is drawn by suction into a mold, which is brought to the surface of the glass.

5. *Gob feeding.* The glass is allowed to flow from a forehearth at a carefully controlled rate, and the necessary amount is sheared off in the form of a "gob."

6. *Drawing.* A sheet or cylinder is drawn continuously and ver-

tically through an orifice in a refractory bar or ring resting on the surface of the glass. In the case of a cylinder, compressed air is employed to maintain uniform diameter as the glass hardens.

7. *Flowing.* The glass flows continuously from a forehearth through an orifice, the shape of the orifice being determined by the product to be made.

Working. Shaping glass into its final form is known as "working." The earliest method of glass working and one that is still used to a surprising extent is "offhand" working. Very great skill and dexterity is required on the part of the operators. The glass is gathered on a blow iron, and by a combination of blowing, rolling the iron on the two arms of a chair, swinging, and shaping by means of wooden tools, the article is given its shape. The article may be returned at intervals to a furnace, known as a "glory hole," for reheating. When shaping operations are practically complete, the article is cracked from the iron, the top cut off, and the edge smoothed, rounded, or flared as desired. A great deal of "art glass" is made by offhand methods.

The use of blow molds is often combined with offhand methods. The glass on the end of the blow iron is worked by swinging, rolling, and blowing until it is in satisfactory form known as a "parison," and is then placed between the open halves of a mold, the mold is closed, and the article is blown with continuous rotation of the blow iron. Flasks, beakers, and funnels are commonly made by this method. In each case the upper portion is cut off and the rim or neck is reheated and shaped as desired.

Gobs gathered on a punty iron are dropped into press molds, the mold giving the outer form and the plunger the inner form. Rotation eliminates marks due to the small space between the two halves of the mold, but obviously a raised design prevents rotation.

A great variety of machines have been devised for making jars, bottles, tumblers, bulbs, and similar hollow ware. In some of these machines the glass is delivered as a gob, which is subsequently pressed or pressed and blown into final form. In others the glass is gathered by vacuum into a mold and subsequently blown into its finished shape in another mold. It is interesting to note that until very recently automatic machines imitated very closely the movements of offhand working. At first the glass was gathered by hand and fed into the machine. Automatic gathering or feeding followed. Ultimately, hand methods were practically forgotten and machines were designed on the basis of the simplest and most direct method of handling and working the glass. The Corning bulb machine, the most recent of all automatic

machines, combines speed of production with simplicity. It is capable of turning out 450 of the smaller sizes of electric light bulbs per minute. An editorial staff report, which appeared in the June 1932 issue of *Chemical and Metallurgical Engineering*, describes the operation of this machine and should be read by all who are interested in glass technology. In this machine a stream of glass from a forehearth flows between two cylinders, one plain and the other with recesses about four inches apart, which form a thin ribbon of glass on which are a series of disks. These have been variously likened to poached eggs or to toy pistol caps on a ribbon of paper. The ribbon descends upon a horizontal conveyor made up of perforated plates hinged together, the

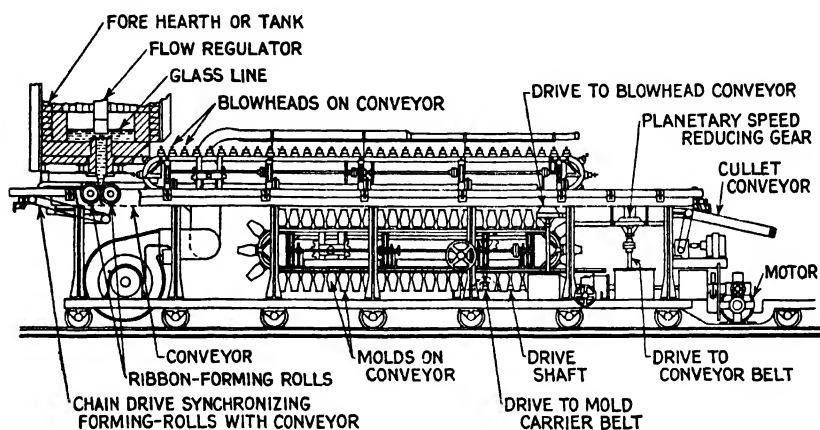


FIG. 70.—Corning Bulb Machine. Courtesy *The Glass Industry*.

perforations registering exactly with the disks. Almost immediately the mouths of a series of blowheads on a conveyor make contacts with the disks and follow them for a good part of the length of the machine. As each disk sags through a hole in the conveyor, it is first blown to form a sort of "test tube," and then a mold closes around it. These molds, like the blowheads, are on a conveyor. A gentle pressure blows the glass to the walls of the mold, which spins on its axis. When the operation of blowing is complete, each mold is opened, returns inverted, and is cooled. The ribbon of glass carrying partially finished bulbs passes an oscillating flap of metal which breaks each bulb off and drops it upon a belt. This in turn deposits the bulb on a conveyor made up of two steel ribbons traveling at different speeds, which spin the bulb neck down between the flames to relieve strains. The bulbs are then cooled on a belt and are examined, frosted if necessary, and packed.

The ribbon of glass from which the bulbs have been removed is dropped on a conveyor and returns as cullet to the melting tank. More com-

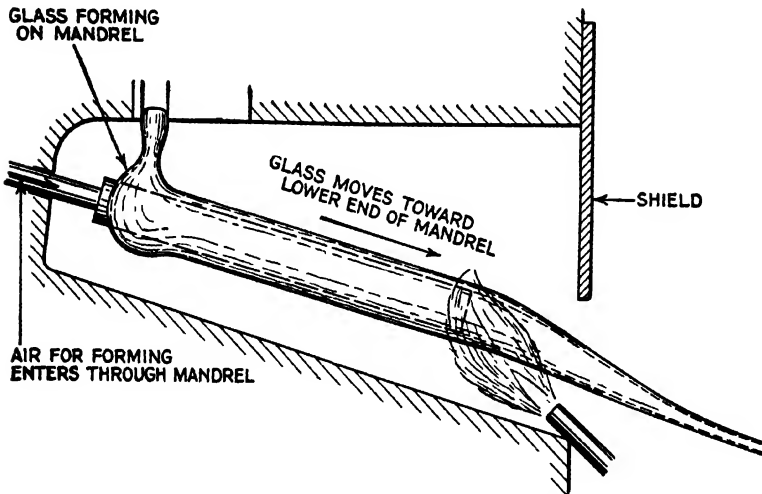


FIG. 71.—Drawing Glass Tubing. Courtesy Corning Glass Works, Corning, N. Y.

plete descriptions of this machine are available in *The Glass Industry*, Vol. 12 (1931), 159–165 (by F. W. Preston), and *Chemical and*

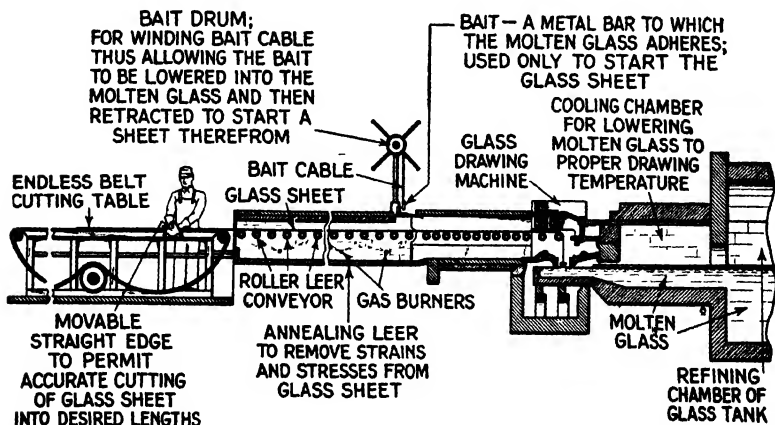


FIG. 72.—Drawing Sheet Glass. Courtesy Libbey-Owens-Ford Glass Company, Toledo, Ohio.

Metallurgical Engineering, 39 (1932), 310. This machine is portable and is mounted on wheels. Within ten minutes it may be moved away

from a tank and another put in its place, so that repairs may be made, or another size of mold substituted.

Tubing was originally made by gathering and blowing a thick-walled bulb, attaching a second iron to the end of the bulb, and drawing the glass to the desired size. Tubing is now also made continuously by allowing glass to flow around a rotating, hollow, clay mandrel and thence through an orifice, admitting air to the center of the mandrel, and drawing at an accurately measured and uniform rate for a distance of some 150 feet. Rods are made in the same way, the use of air being omitted.

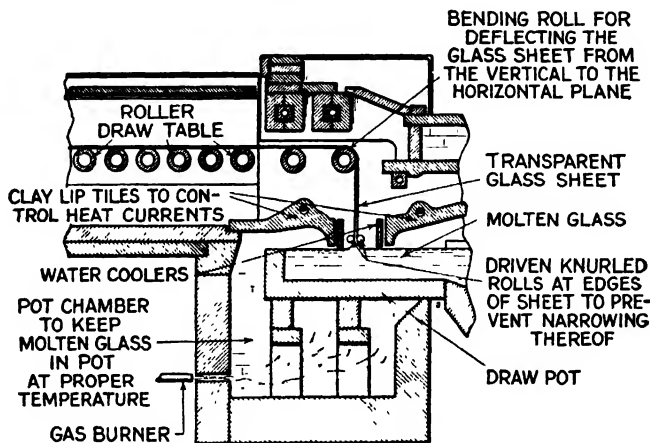


FIG. 73.—Removal of Glass from Draw Pot (See Fig. 72). Courtesy Libbey-Owens-Ford Glass Company, Toledo, Ohio.

The oldest method of making sheet glass was to gather and work the glass by offhand methods into a cylinder with closed ends. The ends were cut off, and the cylinder split and flattened in a reheating furnace. The next step was to draw the cylinder through an annular orifice, the resulting cylinders often being 2½ ft. in diameter and 30 to 40 ft. high. The cylinder method is being superseded by those which draw a continuous sheet or ribbon of glass from an orifice.

Glass may be formed into thick sheets by pouring molten glass on an iron table with raised edges and rolling into form with an iron cylinder. Plate glass is made by pouring, rolling, and annealing, followed by long and tedious grinding and polishing operations with the cold glass. Plate-glass making was originally a batch operation but is now a continuous one, involving the flow of the molten glass on tables, rolling it, and passing the long sheets through annealing ovens.

Wire glass is made by placing coarse mesh screen wire on one sheet of glass and rolling another sheet on it.

Annealing. After any process of working, the glass must be cooled slowly to atmospheric temperature to avoid setting up harmful strains. If the ware is at a temperature above the annealing point, it is slowly cooled. If the working process has previously cooled the ware below this temperature, it must be reheated and then carefully cooled. The articles are placed in large ovens, or more commonly are drawn through tunnels on trucks or chain belts. All annealing equipment, whether intermittent or continuous, bears the general name of "lehr" or "leer." The temperature in lehrs is very carefully controlled. Strains in glass are easily detected by the use of polarized light, the strained portions being characterized by streaks and bands, but the direction and magnitude of the strains are not clearly shown, and the device is still a qualitative instrument.

After the articles have been annealed and cooled, they are inspected. All imperfect pieces are thrown aside to be crushed and remelted as cullet; the main product goes into storage, and thence to packing and shipping rooms.

Special Glasses. Safety glass consists of the two sheets of annealed and finished glass between which is a layer of transparent nitrocellulose, the whole being cemented together under pressure.

Optical glass is made in the finest grade of porcelain pots with continual stirring of their contents. The glass is now commonly poured very much after the fashion of plate glass, cut into sections, annealed, and ground to form. The chief requirement of optical glass is absolute homogeneity and freedom from even the slightest strains.

Laboratory glassware must be highly resistant to chemical action, and must have a low coefficient of expansion to prevent strains and cracking under sudden changes of temperature. At one time all laboratory glass was made in Europe, but in recent years a very high grade of material is being made in the United States. There is a large and growing tendency to use a sodium aluminum borosilicate glass with a very high softening point. This glass requires the use of oxygen-air mixtures rather than air alone in the blast lamp, but this slight inconvenience is more than compensated by the ease with which the glass is worked, and the practically complete elimination of annealing precautions required for ordinary laboratory glass.

FUSED SILICA

It might be said that the ideal glass is fused silica, because of its low coefficient of expansion, its chemical resistivity, its permeability to ultraviolet light, its great electrical insulating value, and its retention of strength at temperatures up to 1100°C . and even higher. Because of the very high temperature required to get silica in the form of a plastic mass and the impossibility of its ever being heated sufficiently to cause it to flow readily, it is necessary for most purposes to add to silica certain substances such as lime and soda in order to produce a material that can be worked, shaped, and formed at lower temperatures. However, there are certain uses to which commercial glass cannot be put. To meet this demand the very important fused silica industry has been developed.

There is no material that can be used with fused silica at temperatures of the order of 2000°C . At this temperature silica is highly acidic. Basic oxides such as lime and magnesia are out of the question, and alumina would be strongly attacked. It is not only a matter of resistance to chemical attack, but also of purity, since the product must not contain more than 0.1% of any other substance than silica, and action on refractories would mean contamination. The raw materials used are either a sand of 99.9% silica content or rock crystal, a very pure form of silica. This problem has been solved by making the raw material the container for the molten silica. The most common method of melting silica is by the use of an electrical resistance type of furnace. Between two graphite electrodes is a graphite rod, which functions as the resistor. Around the resistor and the ends of the electrodes is piled the raw material in the form of a sand. The sand may be confined in a steel box, but no melt ever comes in contact with the metal, and for practical purposes the furnace may be visualized as a pile of sand into opposite sides of which are thrust two electrodes having between them a resistor. As the current flows and heat is produced, the silica next to the resistor melts and a small amount vaporizes. There is thus a small space between the resistor and the furnace charge, and in this way the formation of silicon carbide is avoided. As heating continues, the resistor is surrounded by a plastic mass of fused silica at a temperature of 2000°C . or more. It is very viscous and therefore does not flow under the influence of gravity, so that the thickness of the fused mass is about the same in all radial directions from the resistor. Around the fused material are

sand grains that are merely sintered together, and around these is the unchanged granular material.

When a "sausage" of sufficient thickness has been melted, one electrode and the resistor are withdrawn, a special type of tongs inserted, and this end of the tube of fused silica is closed by a combination of pinching and lapping. The second electrode is withdrawn and a graphite tube put in its place, the fused material being squeezed very tightly around it. The material is lifted from the bed of sand and very quickly worked into form. In general, the working of fused silica resembles the working of glass except for certain limitations. It will not flow of itself, but must be forced into its final form, either by blowing or pressing. Articles of the general form of flasks are blown in iron molds. The handling is extremely rapid and the molds are quickly removed so that metal molds can be used, often without water cooling. A large number of small articles such as dishes and crucibles are made at the same time by lining the molds with a series of depressions of the outside form of the desired articles. In order to make small tubing of uniform dimensions, the tube first produced is withdrawn, cooled, and ground to uniform thickness. It is then reheated in a tubular furnace, the graphite walls of which are the resistor, until it is sufficiently soft, and is then drawn to the correct dimensions. Silica has the fortunate property of retaining the same relative dimensions of bore and wall thickness during the drawing operation.

Another method is used, particularly where the closed tube (corresponding to the "gob" collected from a glass tank) needs to be thicker at one point than another. This involves heating the previously formed tube in an electric arc and dropping sand or ground rock crystal on it, thereby building it up at the desired point.

Most fused silica is opaque, because of numerous small bubbles of air. No amount of heating and long standing will bring about clearing, as in the glass tank. For most purposes this opacity does not constitute an objection, but when transparent silica is desired the melting is caused to take place under reduced pressure to remove as much air as possible from around the sand grains. By the sudden application of pressure, the small bubbles of gas under very low pressure are made to collapse and are so small as to be invisible and without effect on the optical properties of the materials.

Except in cases when welds have been made, which require very special care, no annealing is required. The articles as they come from the molds are still white hot, and are laid aside to cool. Because of the low coefficient of expansion of fused silica, no strains are set up.

The outer surface of molded articles of fused silica may be smoothed by grinding, but in order to get the same smooth finish as that of glass or glazed ceramic ware, it is necessary to remelt the surface. This is readily done by moving the article under a "three point" electric arc until the outer layer melts and becomes smooth.

The use of fused silica in chemical industry has been discussed in the chapter on Materials of Construction. In addition to these uses, articles of fused silica find a place as insulators in the electrical industry, in radiotherapeutic and ultraviolet light apparatus, in high-power wireless valves, in heat-proof globes and bowls in the lighting industry, and in optical equipment where transparency to ultraviolet light and freedom from distortion with temperature changes are necessary.

VITREOUS ENAMELS

The term "vitreous enamels" refers to silicate materials that have been fused at a bright red heat on metals, serving as protective coatings. Vitreous enamels are not glasses in the strictest sense of the word, but are closely akin to these materials. They contain not only the common ingredients of borosilicate glasses, including silica, boric acid, compounds of sodium, potassium, calcium, aluminum, and sometimes lead, zinc, and barium, but also materials that give additional strength, gloss, and color.

The application of vitreous enamels to metals presents difficulties in that the metals are good conductors of heat, are usually ductile and malleable as well as resistant to shock, and have relatively high expansion coefficients, whereas enamels are poor conductors of heat, are inclined to be hard and brittle, and have relatively low expansion coefficients.

The first stage in the preparation of enamels is essentially the same as that of making glass. The raw materials are melted in a glass tank furnace at temperatures of the order of 2500° F. The molten material is run into a tank of cold water, and the rapidly chilled glass shatters into small particles to form what is known as a "frit." The frit is ground wet with various pigments and with clay of a grade and quality known as "enameler's clay." The product is finally very carefully screened.

There are two processes of applying enamels to metals. The "dry" process involves sprinkling the enamel material in the form of a dry powder on the heated metal and placing the article in a furnace. Additional coats are put on in the same way. The "wet" process

includes application of the enameling materials in the form of a suspension in water by a spraying or dipping process, draining and drying the coated article, and burning on the enamel in a furnace.

Vitreous enamels are applied in some cases as a single coat, but it is very common practice to apply and burn on a ground coat, and to cover this with "cover coats." If the enamel is colored, the coloring material is commonly only in the cover coats.

The metal to be coated is for the most part iron or iron alloy, including "ingot iron," which is commercially pure iron, sheet metal, and commercial gray cast iron. The surface must be thoroughly cleaned, and this is accomplished by means of a sand blast, dilute sulfuric acid and hot alkaline solutions.

Burning is usually done in muffle furnaces heated by gas, oil, or coal. Electrically heated furnaces are not of the muffle type, since there are no products of combustion from which the ware is to be protected. The temperature is very carefully controlled and is of the order of 1575° F. to 1600° F. for ground coats and from 50 to 100 degrees lower for cover coats. The time of burning varies from 4 minutes for sheet metal up to 15 minutes for thicker materials.

Enameled-metal products include a great variety of articles, such as sanitary ware, table tops, refrigerator linings, trays, scales, stoves, food storage tanks, and cooking utensils.

CLAY PRODUCTS

The second division of silicate industries includes materials that are molded when in a wet and plastic condition, dried, and given permanent strength by being heated to a sufficient temperature to bring about vitrification. The materials used are commonly known as clays.

The ceramics industries are primarily interested in the physical and chemical properties of clays, and recognize a number of types. Among them a few may be mentioned as typical. Ball clays represent the maximum degree of subdivision and the greatest degree of plasticity. Kaolin is a general term referring to an amorphous material whose composition corresponds to the formula $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$. China clay is a comparatively pure commercial variety of kaolin. What is known as "kaolinite" has the same formula as kaolin, but is composed of worn and rounded crystals. Basaltic clays are the result of the weathering of basaltic rock, and there are clays that have been formed from volcanic ash. Material that was formerly plastic may have become a

hardened gel. Shales are made up of strata of clay that have been highly compressed and heated, but not to the extent of vitrification.

From a chemical standpoint, clays are primarily regarded as made up of the oxides of silicon, aluminum, iron, magnesium, calcium, and sodium in combination with each other and with water. Titanium dioxide and various other substances are present in minor amounts. The ceramist is able to tell from an ultimate analysis something of the amount of kaolin present, the approximate refractory nature of the final product, and the approximate "fired" color. The interpretation is difficult and not always accurate. Soluble salts are of special importance, particularly calcium sulfate. These salts are not wholly decomposed in firing, and are brought to the surface of brick by rainwater, making unsightly "salt stains," and also having unfortunate action on the undercoatings for glazes.

The physical characteristics of clays are of great importance. Two clays which give the same chemical analysis may be utterly unlike when fired. A common method of determining the firing characteristics of a clay is to mold it into a cone of the same form and type as a pyrometric cone, heat it under known conditions, and observe its behavior.

Plasticity is an important property of clays. A viscous liquid is differentiated from a plastic solid in that the former flows, theoretically at least, with the application of an infinitely small force, whereas the latter will not flow until the pressure has passed a certain point known as "yield value." Plasticity is explained on such grounds as surface tension, molecular attraction, and colloidal condition.

Clays behave in much the same way as hydrous silica, hydrous alumina, gelatin, and glue, their properties being those of matter in the colloidal condition. Pure clay in pure water has the same *pH* value as the water. The *pH* values of clays depend on the amount of adsorbed salts, and their isoelectric points vary according to the nature of the dispersed phase in colloidal suspensions. The colloidal characteristics of clays change with time. Various organic compounds have profound effects on these characteristics, and this is one of the explanations of the changes of clays when aged.

A certain amount of non-plastic material is necessary in the making of clay products. A part of this is present as natural mineral impurities and a part is added as "grog" or ground burnt clay. If it were not for this non-plastic material, clay could not be shaped, dried, or fired. It would take up too much water, become too sticky, and crack on drying and firing.

The various refining operations to which clays are subjected include mechanical disintegration, both dry in rolls and pan mills and wet in pan mills; suspension of the finely ground material in water by means of stirrers in vats, this being aided by change of pH value by means of alkali; flotation for the removal of coarse sand; classification to remove grit; coagulation by the use of acid to the isoelectric point; screening, settling, decantation, filtration; and drying.

The product of the filters, which are commonly of the plate and frame variety, is mixed with grog in mixers known as "pug mills." These mills are essentially covered troughs equipped with stirring blades on a shaft, which serve not only to mix the product, but also to force it out through a restricted opening at the end. The clay is often allowed to age for several months before it is formed, dried, and burned. This aging process involves storage of the clay in damp cellars. Part of the effect is probably hydration with the formation of a more plastic material. Bacteria probably form organic acids, the organic matter originally in the clay serving as food for the bacteria.

Clay ware may be formed by hand, either with or without the use of a revolving table known as the "potter's wheel," various shaping tools being employed. Molds are very common in this industry. Porous molds receive a suspension of the clay known as "slip" and take up the excess water. Non-porous molds use a clay with just enough water to enable it to be handled. Where the shape permits, the article may be formed by a plunger revolving within a mold. A "jigger" is a mold that gives the outer form to the ware; the inner form is produced by cutting and shaping tools. Pipe is made by forcing clay through a ring-shaped opening. Brick and tile are either molded in forms, or formed by forcing the clay through a die as a bar, or as a tube with the same inner shape as the tile, later being cut into convenient lengths.

After the ware is formed it is common practice to apply a "glaze," if a smooth finish is desired, before the ware is dried and burned, hence glazes may be discussed briefly at this point. Glazes are essentially glasses, which are melted on the surface of ceramic ware, usually during the main burning operation. They serve mainly to give a smooth surface to the ware, and in many cases also perform the added function of rendering a porous material impermeable to liquids by covering it with an impermeable surface layer. In order to secure an adequate bond the ware is coated with a thin layer of clay that will partially fuse at the highest kiln temperature, and the glazing material is applied to this. It is often necessary to suspend finely ground frit in water as

a thin paste, before applying, the procedure being the same as in vitreous enameling. Where the glaze has the same color as the ware, it is common practice to tint the glaze with an organic dye, which burns out readily in the kiln. Colored glazes are of the same general nature as colored glass. Decorations may be under a transparent glaze, or may be burned on with the glaze. The cheapest and simplest glaze is obtained by throwing sodium chloride into the kiln while the ware is being burned. Fused sodium aluminum silicates are formed on the surface. Burned ware may also be covered with the glazing material, the articles redried, and the final burning carried out in a separate kiln known as "glost" kiln.

The articles made of damp and plastic clay must be very carefully dried. The water moves to the surface by capillarity to take the place of that removed by evaporation. It is necessary to regulate the rate of drying very carefully, since the article shrinks as it loses water, the amount of shrinkage being between 8% and 12%. If evaporation takes place more rapidly than the water can be supplied to the surface by capillarity, the article will crack. Strains may also be set up. Heat is supplied either by waste flue gases or by passing air over steam coils. Temperature and humidity are accurately controlled during the drying operation.

The following changes take place during the burning process. Drying has removed a considerable part of the water, and the exterior of the article is relatively hard, while the inside is somewhat plastic. The first step is the removal of the mechanically held water, a period known as "water smoking," which extends until a temperature of around 150° C. is reached. This is followed by the breaking up of hydrates and the removal of chemically combined water. This removal is not complete until a temperature of the order of 600° C. has been reached.

At about 350° C., oxidation begins and continues to an upper limit of 950° C. If the carbon content of the clay is high, oxidation of sulfur and iron is considerably retarded. Iron sulfide in clay is oxidized to sulfate, and this in turn breaks up into ferric oxide and sulfur trioxide. Carbon serves to reduce sulfates to sulfides again. There is comparatively little absorption of sulfur trioxide from flue gases, but in some cases there is enough to give efflorescent sulfates in the finished product.

At 900° C. or thereabouts vitrification begins. Anhydrous aluminum silicate, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, dissociates into silica and amorphous mullite, the latter crystallizing later when cooled. Mullite has the formula

$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and is unique in that it can crystallize readily. It develops in all types of vitrified ceramic bodies and from molten liquids even if chilled by quenching. When fusion begins, the surface tension of the liquid formed causes a certain amount of contraction as well as change in free pore space. The pore space during the dehydration-oxidation period increases somewhat, but when vitrification begins the pore space decreases. Unless the article is overfired, the exterior volume reaches a minimum value. Excessive firing means deformation of shape and expansion due to escape of gases.

In addition to the changes that take place in the silicates, there is decomposition of calcium carbonate at 800°C . Calcium sulfate is not completely decomposed until a temperature of 1325°C . is reached, which is higher than the proper firing temperature of many clays.

The changes that take place during vitrification are extremely complex. Elaborate phase rule studies have been made of all possible combinations of silica, alumina, lime, and magnesia. The oxides of calcium, magnesium, zinc, and barium have very high refractory qualities when alone, but with silica and alumina they form glasses of lower softening point, and at correct concentrations they form eutectics. Other oxides such as those of lead, sodium, potassium, and boron are powerful fluxes, greatly lowering the point at which fusion takes place. Feldspar is a flux that requires a higher temperature before it becomes effective. These materials provide a liquid in which the refractory portions of the clay tend to dissolve, and the matter of formation of eutectics is of minor importance. The greater the quantity of fused material and the greater the fluidity, the narrower is the vitrification zone. On the other hand, a very viscous flux retards interaction and gives a broader vitrification zone. The upper limit to which the ware is heated depends on its composition and the physical properties of the clay from which it was formed. Warping must be avoided, and the product should be brought to the desired volume, specific gravity, and porosity. Some wares depend for their strength on interlocked crystals, but for the most part strength is due to fused material between individual grains.

Color in ordinary clay products is due primarily to iron. Under oxidizing conditions, iron produces a red color, but under reducing conditions the color is gray. The color produced is also influenced by size and distribution of grains and the amount of lime, alumina, and fluxes. Manganese dioxide gives black spots in the product, this effect often being sought for in face brick. Other colors are ordinarily in the glaze rather than in the body of the ware.

The peculiar requirements of heat-resisting ceramic products should be noted in this connection. Clay refractories are made from materials very high in true clay substance and as free as possible from fluxes. There are comparatively few plastic clays that will yield products of high refractory quality. Sillimanite, $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, is an extremely refractory material, having a melting point of 1750°C . Kaolin, though having lower refractory value, is the most common material used for making heat-resisting products. Siliceous clays having a silica content of 70% or more make very rigid refractories. For some purposes the fresh clay is mixed with as much as its own weight of grog. In general, refractories are refined, molded, dried, and burned as ordinary clays. A noteworthy exception is the production of mullite bricks or blocks. A crystalline material is obtained from the fusion of raw materials in an electric furnace, which is ground, molded, dried, and reburned. Clay is used to some extent as a bond in making silica brick, but for this purpose it is less used than lime. Small amounts are used in making aluminous refractories.

Most brick and tile are burned in intermittent kilns, but the use of ring kilns is increasing in the ceramic industry. Larger plants are beginning to install tunnel kilns. Since these three types of kilns are used very little except in the ceramic industry, they are described here rather than in the chapter dealing with unit chemical engineering operations.

An intermittent kiln is essentially a chamber of firebrick, usually circular in cross section and with a dome-shaped refractory roof. The flames enter at a series of ports near the floor of the kiln, being deflected upward by low walls, and also through openings in the floor, thus causing the roof to become intensely hot and to reflect radiant heat on the ware. The hot gases pass down through the ware, and through openings in the floor to the stack. The material is thus heated both by direct contact with the gases and by radiation from the roof and walls of the kiln. When the burning is complete, the ware is cooled slowly, air ultimately being admitted through an opening in the door of the kiln, which was closed with firebrick during the firing operation. This opening is gradually enlarged until the door is entirely clear by the time the ware is cool and ready to be removed.

The ring kiln is essentially a series of intermittent kilns, which are operated on a definite cycle, which use hot finished ware to preheat the air necessary for the combustion of the fuel fed to a single kiln at a time, and which preheat the unburned ware by the waste gases before their final discharge. There are thus openings from each kiln to the

next one on each side. During operation all these are open except the one between the kiln which is being discharged and the one next to it, which has been freshly charged with green ware and which is connected with the stack.

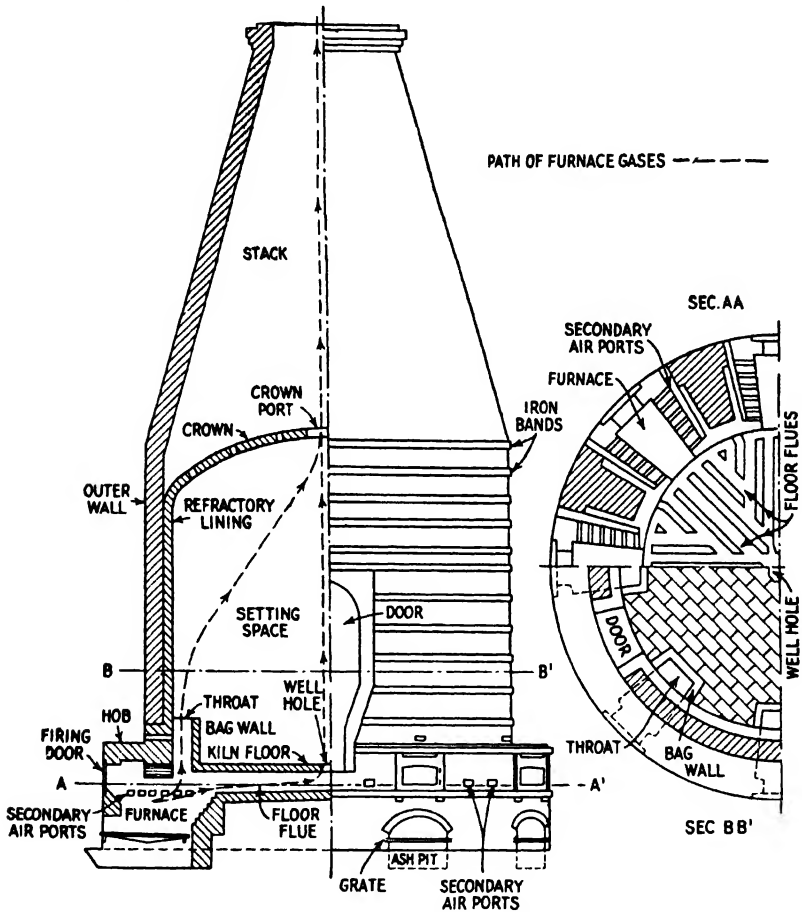


FIG. 74.—Up-Draft Intermittent Kiln. Courtesy Professor R. G. Mills, Department of Ceramics, Rutgers University.

The tunnel kiln is operated continuously, green ware being fed at one end and burned and cooled ware being removed at the other. The kiln is essentially a long tunnel of refractory material, equipped with ducts for handling the air and waste gases. The cars or trucks on which the ware is conveyed are made of firebrick slabs. The steel track and wheels of the trucks are protected both by the heat insula-

tion of the thick floor of the trucks, and also by the projecting sides of the floor as they drag through troughs of sand on each side of the tracks. As the green ware enters, it is warmed up gradually and finally heated very strongly by the hot waste gases. In the combustion zone, gas is introduced from ports, mixed with preheated air, and burned. As the hot ware moves out of this zone, air passes over it counter current, cooling the ware and being itself preheated.

Among common clay products may be mentioned such structural materials as brick, tile, and terra cotta; pottery, including table,

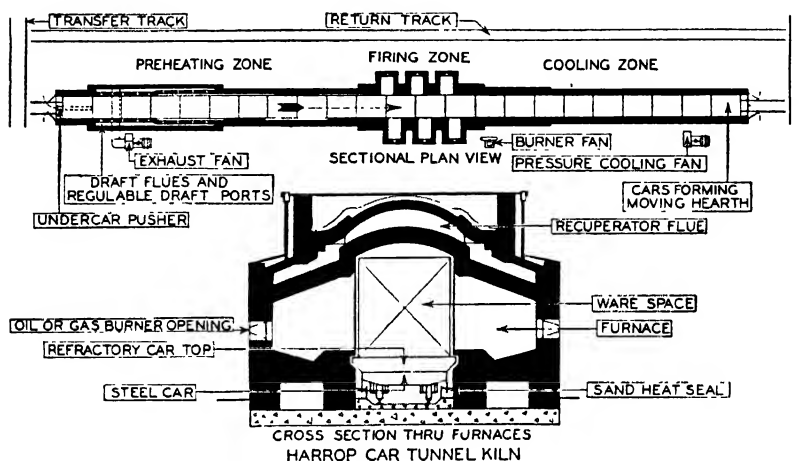


FIG. 75.—Harrop Car Tunnel Kiln. Courtesy Harrop Ceramic Service Company, Columbus, Ohio.

kitchen, art, and sanitary ware, stoneware, and chemical porcelain; electrical porcelain; and refractories.

PORTLAND CEMENT

Although the calcium compounds are greater in quantity than any other substances present in portland cement, the fact that the most abundant and important of these compounds are calcium silicates is justification for the inclusion of portland cement as a silicate industry.

The *official* definition of portland cement is as follows: "Portland cement is the product obtained by finely pulverizing clinker made by calcining to incipient fusion an intimate and properly proportioned mixture of argillaceous and calcareous materials, with no additions subsequent to calcination excepting water and calcined or uncalcined

gypsum." A somewhat simpler definition has been given in these words: "Portland cement is a finely pulverized material consisting of certain definite compounds of lime, alumina, and silica, which when mixed with water has the property of combining slowly with the water to form a hard, solid mass."

The name is due to some resemblance of the product to a building stone quarried in the Isle of Portland in England. Much of the early work in this field was characterized by great secrecy, and it is very difficult to assign proper credit to pioneer workers in this field.

For many years cement was made from rock called "cement rock" which contained lime, alumina, and silica together with ferric oxide and magnesia in proportions which resulted in a cement of commercial value. Natural cements differ from portland cements in that they are made by burning argillaceous limestones at a temperature much lower than is required for the clinkering of portland cement mixtures.

Portland cement was first used in the United States in sidewalk construction, and then in the foundations of buildings. Its better adaptability to winter construction caused it to be favored over natural cement, and ultimately the latter was completely displaced.

For a number of years all portland cement was imported, and even after manufacture began in the United States the domestic product often bore foreign labels. As early as 1888 nearly two million barrels of portland cement were imported yearly into the United States. In 1904 the domestic production was over seventeen million barrels. In 1928 over 178 million barrels of cement were made in the United States, which represents a maximum in the history of the industry.

Portland cement, when mixed with water, forms a plastic paste. When this paste is mixed with sand, screenings, or other fine aggregate, the mixture is known as mortar. If, in addition, gravel, crushed stone, or other coarse aggregate is introduced, the product is known as concrete. In order to make a satisfactory concrete the mixture of cement, sand, rock, and water should be "plastic, homogeneous, freely but sluggishly mobile, and free of segregation as far as the law of gravity permits." The ideal to be approached in concrete is that the total volume should be the sum of the volumes of the materials, that is, that the cement should fill all voids. Both fine and coarse aggregates should consist of mixed sizes ranging from very fine to $\frac{1}{8}$ or $\frac{1}{4}$ in. diameter for fine and from $\frac{1}{4}$ to $1\frac{1}{2}$ in. for coarse aggregate. In massive work with little or no reinforcing steel, much larger coarse aggregate can be used. The proportions of cement, sand, and rock depend on the quality and use expected of the concrete. In general,

the proportions vary from cement 1, sand 1, and rock 2 for thin water-tight sections, to cement 1, sand 3, and rock 5 for concrete that is not necessarily water-tight, and which does not have to bear heavy loads. The quantity of water is extremely important. If this quantity is too low for given proportions, the mixture will not fill the corners of the molds and the paste itself is granular and lacks plasticity. Too much water allows segregation of aggregates and leads to weakness and excessive disintegration of the concrete when exposed to the weather. In order to have a water-tight concrete the paste must fill all the spaces. In order to get a mixture that can be satisfactorily placed, more water is used than is needed for chemical combination with the cement to cause setting and hardening or what is called "curing." The remaining water must be removed by evaporation. The volume of water in gallons is approximately the same as the number of cubic feet occupied by the sand and coarse aggregate. The first five to ten days of curing require that the mixture shall remain moist.

Curing is greatly retarded by low temperatures on account of the low velocity of the necessary chemical reactions between the cement and water. Freezing results in concrete of greatly lowered quality and strength. This is due to the great retardation of setting and hardening because of the low temperature and the removal of forms before strength is attained. Care is commonly taken to maintain sufficiently high temperatures for the first few days to permit considerable hardening.

The strength of concrete depends primarily on the strength of the hardened cement paste. This involves the cement itself, the water-cement ratio, and the extent to which the reactions of hardening have progressed. Compressive strengths in common use vary from 2000 to 5000 lb. per square inch at 28 days with occasional values as high as 10,000 to 12,000 for special uses. Modulus of rupture, which is the common basis for design of pavement slabs, is roughly $\frac{1}{5}$ and tensile strength $\frac{1}{10}$ of compressive strength. Fortunately, however, concrete has essentially the same coefficient of thermal expansion as steel. Hence it is commonly reinforced with corrugated steel bars or rods, so that the steel takes the strain of tension, and the bond between the roughened metal surface and the concrete prevents the steel from being pulled through. Since properly made concrete is water-tight, the steel is protected against corrosion.

The raw materials from which portland cement is made fall into two general classes: *calcareous*, composed largely of calcium carbonate; and *argillaceous*, which are mainly aluminum silicates containing

some iron. Marl, chalk, marine shells, and precipitated calcium carbonate wastes are other sources of the calcium oxide component, and shale, slate, and blast furnace slag may furnish the alumina, ferric oxide, and silica.

A chemical analysis of finished portland cement has some value in showing whether or not the materials were correctly proportioned, but tells nothing about the way the cement was burned. The free lime test is the best chemical method for defining the completeness of burning. There is some variation in the composition of portland cement, but a fair average at the present time is represented as follows.

	PER CENT
Silica (SiO_2)	21.1
Ferric oxide (Fe_2O_3)	2.7
Alumina (Al_2O_3)	5.9
Calcium oxide (CaO)	64.5
Magnesia (MgO)	2.4
Sulfur trioxide (SO_3)	1.7
Loss on ignition	1.5

The lime is higher and the silica lower than in earlier cements.

Until very recent years, all standards regarding the composition of portland cement were the results of practical experience and were developed with only partial knowledge of the compounds actually present. The introduction into the field of cement of the modern methods of physical chemistry, including phase rule studies, microscopic tests, and X-ray identification of compounds, made possible a fairly complete understanding of the composition of portland cement. Among the pioneer investigators in this field were: Tornebohm, who identified by means of petrographic methods certain crystalline constituents, and a glass; Richardson, who advanced the idea of solid solutions; and Campbell and White, who further identified and explained the nature of these solutions.

Certain phase rule studies which have shed important light on the problem were undertaken by the Geophysical Laboratory of the Carnegie Institution at Washington without special application to portland cement. A thorough investigation of the lime-alumina-silica system included the use of about one thousand different mixtures and gave a very clear picture of the entire system. As a by-product of this investigation the limited area represented by portland cement clinker was very thoroughly studied, and it was found that on a three-component diagram it fell in the region where only three compounds could exist under equilibrium conditions. These were tricalcium silicate,

$3\text{CaO} \cdot \text{SiO}_2$, dicalcium silicate, $2\text{CaO} \cdot \text{SiO}_2$, and tricalcium aluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. A satisfactory white cement could be made by burning those proportions of lime, alumina, and silica which would give the three compounds, but temperatures above the economical commercial range were required.

The attention of the portland cement industry was directed to the value of this type of work, and under the auspices of the Portland Cement Association a great deal of very valuable research has been carried out on the composition and mechanism of formation and subsequent reactions of the substances forming portland cement.

Iron oxide plays a part in compound formation in portland cement manufacture, and magnesium oxide is always present along with minor amounts of alkalies and titanium oxide. The five important compounds shown by the most recent work in this field to be present in portland cement clinker are:

Tricalcium silicate, $3\text{CaO} \cdot \text{SiO}_2$.

Dicalcium silicate (beta), $2\text{CaO} \cdot \text{SiO}_2$.

Tricalcium aluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$.

Tetracalcium aluminoferrite, $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$.

Magnesium oxide, MgO .

These substances can be detected individually by X-ray methods, the lines corresponding to those of pure substances prepared by methods of proved reliability. Phase rule studies by means of cooling curves, and both microscopic and chemical methods, give ample confirmatory evidence of the presence of each. Methods of calculating their amounts have been worked out which check very closely the values obtained by various methods of detection and estimation. Free lime, at one time thought to be an essential component of portland cement, is found by chemical and X-ray methods to be present only in negligible amounts, usually less than 1%. When present in amounts greater than 2% to 3%, the cements may fail to pass the standard specifications by developing unsoundness in an accelerated expansion test. Some investigators have contended that solid solutions are formed of lime or of aluminates with the calcium silicates, but recent exhaustive studies have reported the improbability of the existence in cement of such solutions. Magnesia, which may be present up to 5%, is for the most part uncombined. The amounts of alkalies, titanium dioxide, manganese oxides, and phosphate are so small—not over 2%—as to have very little effect. They are probably present as crystalline compounds whose composition has not yet been determined.

After the burning and cooling of clinker and before final grinding,

calcium sulfate is added for the purpose of regulating and retarding the setting of the finished cement. With this addition the major compounds in the final product may be satisfactorily represented in an average cement as follows:

	PER CENT
$3\text{CaO} \cdot \text{SiO}_2$	51
$2\text{CaO} \cdot \text{SiO}_2$..	22
$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	11
$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	8
CaSO_4	2.9
CaO ..	1.0
MgO ..	2.4

Many theories have been advanced to account for the setting and hardening of cement, but none were of much value until the nature of the compounds present in cement clinker had been determined and pure compounds had been made and isolated. Once this had been done, it was possible to examine each compound separately and to see the effect of water and solutions. Michaelis was probably the first to point out the colloidal nature of the setting and hardening processes. The basis of the modern theory accounting for these phenomena is the work of Le Chatelier published in 1887, in which he explained the chemical changes as a series of hydration reactions.

Two types of reaction take place simultaneously when finely ground cement is mixed with water: hydrolysis and hydration. There is clear and abundant evidence that both are extensive and in some cases quite rapid. Some hydration products are crystalline, but others are definitely colloidal.

Tricalcium aluminate hydrates very rapidly to a crystalline material. If this were permitted to take place at its normal rate in the making of concrete the setting would start before the concrete could be properly mixed and placed. Calcium sulfate is therefore added as a retarding agent to prevent a too rapid set. That compound reacts with the tricalcium aluminate to produce calcium sulfo-aluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$. This product is less soluble than tricalcium aluminate hydrate, and it precipitates until all gypsum has been used up. By this time the concrete has been mixed and placed. The remaining tricalcium aluminate then hydrates to crystalline tricalcium aluminate hydrate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$, which causes the initial set of the cement. After a few hours, crystals of calcium hydroxide begin to separate from the supersaturated solution. The initial set requires from one to two hours.

For the first month, the development of strength is due to the formation of colloidal gels. Tricalcium silicate hydrolyzes to form a colloidal silicate of lower basicity and calcium hydroxide, and hydrates to form a colloidal gel. Dicalcium silicate hydrates very slowly and for the first month of the life of the concrete has relatively little effect. Within a period of three months and up to a year, it is probably as efficacious in developing strength as the tricalcium silicate. In saturated calcium hydroxide solution the equilibrium hydrate of dicalcium silicate is probably best represented by the formula $3\text{CaO} \cdot 2\text{SiO}_2 \cdot n \text{H}_2\text{O}$.

Thus it will be seen that the setting and hardening of portland cement consist of a complex set of hydrolysis and hydration reactions with the formation of saturated calcium hydroxide solutions, crystals of calcium hydroxide and of tricalcium aluminate hydrate, and colloidal gels composed of calcium silicates, which ultimately harden.

The manufacture of portland cement comprises a series of chemical engineering operations most of which have been previously described, together with the equipment used. Hence only a very brief discussion of the manufacturing operations is necessary.

The raw materials must be finely pulverized prior to the burning operations. The material is first crushed in gyratory, jaw or roll crushers and then subjected to preliminary grinding in hammer mills or ring-roll mills. Finish grinding may be done by either the wet or dry process. In either case, the machine almost universally used is the tube mill. In the dry process, the crushed material is dried, usually in rotary dryers, to a moisture content of 1% or less. In the wet process, enough water is added to the tube mill feed to give the resulting product a moisture content ranging usually from 32% to 40%. The finely ground raw material produced by the wet process is known as slurry, which is a suspension of such consistency that it can be handled by means of pumps. Where clay is used as a raw material and ground by the wet process it is frequently prepared in a wash mill as a separate suspension, the operation serving to break up lumps and remove coarse sand. In both the wet and the dry processes, closed circuit grinding is a recent development, which is adding to the efficiency of the grinding operation. In the dry process, screens and air separators are used to separate oversize from finished material, the oversize being returned for further grinding. In a few wet-process plants metallurgical type classifiers are used. The excessive amount of water needed in the wet classification operation is removed in traction thickeners. Many wet-process plants reduce the water in the

slurry to 18–20% by means of filters, which are generally of the suction type.

Close chemical control is maintained throughout the grinding and blending processes. Control generally begins with analysis of materials at the quarry, and various parts of the deposit are blended to give a mixture of approximately the correct proportions. The raw materials, after grinding, are sampled and analyzed, and the contents of various storage tanks or bins are blended to give a kiln feed as accurately proportioned as possible.

The most common fuel for burning cement is pulverized coal, although many plants located near sources of oil or natural gas use these fuels. Coal is prepared for use by crushing, drying, and fine grinding to approximately 90% passing 100 mesh. Ball mills and roll mills are most commonly used in this operation. Some processes for circulating dry heated air through the pulverizer have been developed. Practically all the cement made in this country is burned in rotary kilns.

A rotary kiln is a steel cylinder, lined with firebrick, and set at a very slight angle from a horizontal position, the pitch being from 0.5 in. to 0.75 in. per foot. The kiln is equipped with several tires, which run on rollers, and is driven with girth gears. The smaller kilns revolve at a speed of one to two revolutions per minute; very large kilns move more slowly. At the lower end of the kiln is a very short cylinder of firebrick, closed at one end, and somewhat greater in diameter than the kiln, set on wheels so that it may be drawn up close to the kiln, the lower end fitting closely, the kiln turning within it. Through it pass burners for gas or powdered coal, and it is provided with an opening for the discharge of the hot products. A more recent type of kiln combines a clinker cooler with this firing hood. At the upper end the kiln projects through a closely fitting circular opening into a concrete chamber lined with firebrick and connected with the stack. The raw material in the form of dry dust, slurry, or filter cake is fed into the kiln through a spout or screw conveyor, which passes through the chamber into the kiln. Waste heat boilers are often interposed between this chamber and the stack, and many plants obtain all their power in this way. Rotary kilns are never less than 60 ft. long, and may be considerably over 300 ft. long, and vary from 6 to 12 ft. in diameter. Cement kilns are protected from heat loss by layers of brick that are made from diatomaceous earth, the insulating layer being between the steel shell and the firebrick lining. In the section in which the highest temperature is attained, the insulation is omitted

in order to permit some radiation, so that the lining of the kiln will not become fused.

Water is driven out by the hot gases passing to the stack, the first fourth of the distance constituting the drying zone. Carbon dioxide escapes from the calcium carbonate present, leaving calcium oxide. By this time the material is three-fourths of the way down the kiln, and the temperature is up to 1650°F . As the endothermic reaction of decarbonation approaches completion, the mass passes into the hottest zone of the kiln and sinters into small lumps, which are greenish-black when cool. The temperature here is about 2600°F . It is estimated

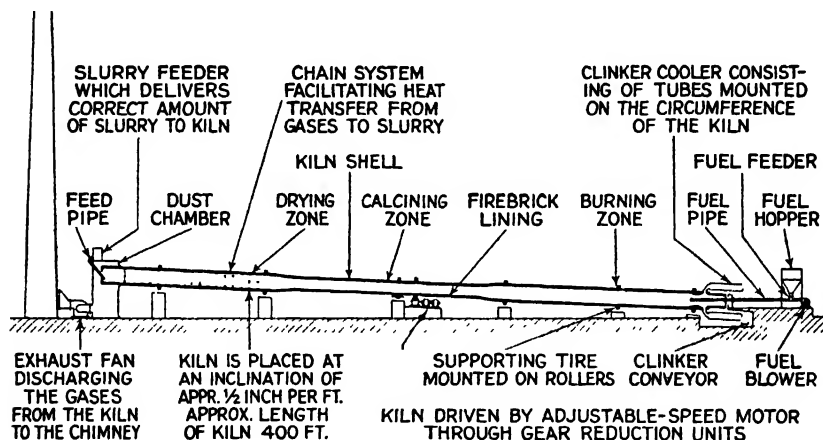


FIG. 76.—Rotary Cement Kiln (F. L. S. Unax). Courtesy F. L. Smidth and Company, New York City.

that 915 B.t.u. are required per pound of clinker. Of this, from 150 to 200 B.t.u. are from the exothermic reactions of clinker formation, the remainder being furnished by the fuel. More than three times this heat is actually developed in the process, from 3000 to 4000 B.t.u. being the estimated heat per pound of clinker. The white-hot clinker drops from the discharge end of the kiln into coolers, which are for the most part rotating shells through which the air for the kiln passes counter current to the flow of the clinker. If coolers are not used the clinker may be spread on the ground by drag chains and sprayed with water. Some hot clinker may be mixed with seasoned clinker to facilitate grinding. Before final grinding from 2.5 to 3.5 lb. of gypsum are added to every hundred pounds of clinker. The clinker and gypsum are ground in mills of the same type as those in which the raw

materials were prepared. Closed-circuit grinding with air separators is now being used to some extent in this operation. The product is finely ground enough to permit 88% to 98% to pass through 200 mesh.

The product is stored in concrete silos, and from these is packed in bags holding 94 lb. Heavy paper bags are rapidly taking the place of cotton or burlap bags, thus eliminating the trouble of returning and reuse of bags, together with the cleaning and repairing necessary. An ingenious folded valve in a lower corner of the paper bag does away with the necessity of tying or sealing the top after filling, the bag being filled from the bottom through the valve.

Although heat recovery is by no means complete, the 60% to 75% of the heat developed by the fuel that would pass up the stack and represent loss has been cut down to such an extent that from 300 to 350 lb. of steam are produced in waste heat boilers for every barrel of cement made, or all the steam needed in the plant. Some heat is also recovered from the hot clinker by passing the air used in the kiln through the coolers. Dust in the air in and around cement plants has been greatly reduced by the increasing use of dust collectors, electrostatic precipitators being the most effective of all dust-recovering equipment in this industry.

CHAPTER XIV

SODIUM, CALCIUM, AND MAGNESIUM COMPOUNDS

The elements sodium, calcium, and magnesium are primarily important in the form of their compounds. The metals themselves have relatively little use in industry, magnesium being the most important. The compounds of these elements are quite numerous, and many of them find extensive use in industry, but discussion will be confined to a few representatives which are sold in great quantities.

SODIUM CHLORIDE

The bulk of all sodium compounds have their origin either directly or indirectly from sodium chloride, common salt. Even naturally occurring sodium salts are in many cases more cheaply produced by chemical means from salt than by refining the natural product. A minor source of salt in this country is ocean water, which contains about 2.9% sodium chloride together with some 0.8% of other soluble salts. In many places in the United States natural brines are obtainable from wells. There are also vast deposits of rock salt of varying degrees of purity. Salt is thus available in unlimited amounts. The production of salt is largely a matter of solution, evaporation, and crystallization. The brine from the salt lakes and from the ocean in regions where evaporation greatly exceeds rainfall is subjected to solar evaporation in large shallow ponds. Calcium sulfate is allowed to precipitate, and the brine is run to another set of ponds. Further evaporation causes the crystallization of sodium chloride in fairly pure form. A "bittern," containing largely magnesium and calcium chlorides, remains but has little or no commercial value.

Rock salt may be mined if the deposit is conveniently located, but otherwise the salt is removed as a brine by pumping water down into the deposit. These artificial brines are the largest source of all salt obtained by evaporation methods.

Some commercial sodium chloride is made from natural brines. They are usually somewhat impure, but the process of evaporation and fractional crystallization is largely depended upon to produce sufficiently pure sodium chloride. Small amounts of lime suffice to coagulate and remove ferrous sulfide and to eliminate hydrogen sulfide.

Some salt is still made in "grainers," which are essentially long, shallow, open troughs heated by steam coils and equipped with reciprocating rakes. The heat efficiency of grainers is low, but they are used because of the peculiar form of salt crystals made, which is in demand for certain uses.

Vacuum evaporators are very generally used in the salt industry, most of these being triple and quadruple effects. Evaporators must be boiled out with fresh water daily to remove salt crystals, and tubes drilled weekly to remove calcium sulfate scale. The evaporators are equipped with settling tanks from which clear liquid is returned and the salt which settles out is centrifuged and dried.

Badger describes a plant that operates with a special process and makes either flat flakes or long needles as desired. The brine is heated under pressure but does not boil. The calcium sulfate is removed mainly by crystallizing in a bed of pebbles, and periodically ground from the pebbles by rotating the container. The hot brine is run through a series of flash vessels where the pressure is relieved by stages. The final crystallization takes place in pans equipped with rakes. The dried and screened material flows freely and is in special demand as table salt.

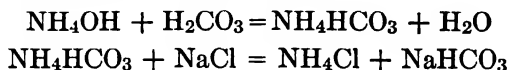
In addition to its extensive use as a source of other sodium compounds and hydrochloric acid, salt is used as a preservative in the packing house and dairy industries, in the preparation of food, as a component of freezing brines, and in the metallurgical, soap, and tanning industries.

SODIUM CARBONATE

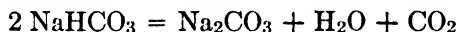
Sodium carbonate is prepared to a somewhat limited extent from natural deposits of "sesquicarbonate of soda," $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3$. It is made largely, however, from sodium chloride. The Leblanc process, used almost exclusively for several decades but now obsolete, consisted essentially of preparing sodium sulfate by the action of sulfuric acid on sodium chloride, reducing the sulfate to sulfide and at the same time converting the sulfide to carbonate by the action of calcium carbonate. Better methods of obtaining chlorine and sulfur, by-products of this process, and high labor and fuel costs caused its final abandonment.

The method now most generally employed for making sodium carbonate was developed in 1863 by Ernst Solvay of Belgium. It depends upon the fact that sodium bicarbonate is the least soluble salt that can be formed in a solution containing sodium, ammonium, chloride, and bicarbonate ions. The process also has the advantage that all mate-

rials used may be pumped as gases, liquids, or suspensions. A saturated brine, after purification with lime and soda, is pumped through towers equipped with cooling coils and with a perforated plate near the bottom. Ammonia gas is bubbled through the brine. The resulting ammoniacal brine is passed downward through bubble towers equipped for cooling counter current to a flow of carbon dioxide. Following are the reactions of the process:



Two towers are commonly used. Sodium bicarbonate appears as a precipitate in the second tower, and the material drawn off at the bottom is a thick suspension of fine crystals of this salt in ammonium chloride solution. The towers are of the order of 70 ft. in height so that both time of contact and pressure thus result. The bicarbonate is removed by the use of continuous rotary filters, and the liquid goes to the recovery system. The gas escaping from the top of the towers, which is mainly nitrogen, is bubbled through brine to remove any traces of ammonia. In one plant this gas is a source of nitrogen for making synthetic ammonia. Since the demand for sodium bicarbonate is limited, the entire product of the towers is converted to the carbonate in a rotary externally heated cylinder. By adding previously calcined soda, caking and corrosion are prevented. The carbon dioxide is added to the kiln gas. The reaction is



Carbon dioxide for the process is obtained by calcining limestone with coke in special kilns which give a gas of at least 30% carbon dioxide concentration, the remainder being mainly nitrogen. The quicklime made at the same time is slaked with ammoniacal liquor, and the slaked lime is used in the recovery of ammonia. Some ammonium chloride is made and sold, but the bulk is returned to the process. The filtrate is run down a fractionating column, and ammonia from ammonium carbonate and bicarbonate is driven out. The hot solution passes down into a still, fed with a suspension of calcium hydroxide. The ammonium chloride is decomposed by the reaction



Calcium chloride is thus the main waste product. Only a part of this finds use in making refrigerating brines and as a dust preventive on roads. In spite of all precautions to prevent the loss of ammonia, it is necessary to add continually fresh supplies of it.

The combination of the direct ammonia synthesis and the Solvay process for making sodium carbonate is employed in some of the large nitrogen fixation plants in Europe, but so far has no special significance in this country.

In the years 1929, 1930, and 1931 the quantity of sodium carbonate made in the United States and its distribution were as follows:

USES	1000 TONS		
	1929	1930	1931
Glass works.....	672	590	519
Chemicals.....	335	290	260
Soap.....	213	200	195
Cleanders and modified sodas. . .	125	112	100
Pulp and paper.	110	100	87
Water softening.....	60	55	50
Textiles.....	40	30	31
Exports.....	40	36	28
Petroleum refining	18	16	15
Miscellaneous	47	40	35
	1660	1469	1320

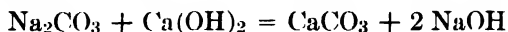
Sodium carbonate appears on the market in two forms: soda ash, which is the anhydrous salt; and a crystalline variety, which is made up mainly of the decahydrate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. Most sodium carbonate used in the industry is in the form of soda ash.

SODIUM HYDROXIDE

Electrolysis of sodium chloride solutions results in chlorine, hydrogen, and a solution of sodium hydroxide. The most widely used types of chlorine cell decompose only a part of the sodium chloride, so that the cell effluent must be concentrated in multiple effect evaporators with separate settling tanks for salt removal in order to obtain a solution of sodium hydroxide free from salt. Mercury cathode cells produce a pure solution of sodium hydroxide but are quite limited in their use.

In any process of electrolysis of brine, the chlorine should probably be considered the main product, and sodium hydroxide and hydrogen by-products, since it is cheaper to make sodium hydroxide by the causticization method. If a solution of sodium carbonate is heated

and a suspension of calcium hydroxide added, a precipitate of calcium carbonate will be formed, while the liquid that separates is mainly a solution of sodium hydroxide. The reaction is as follows:



Both batch and continuous methods are used, but the latter are increasing in importance. In the batch method the reaction is carried out at the temperature of boiling water either in insulated tanks

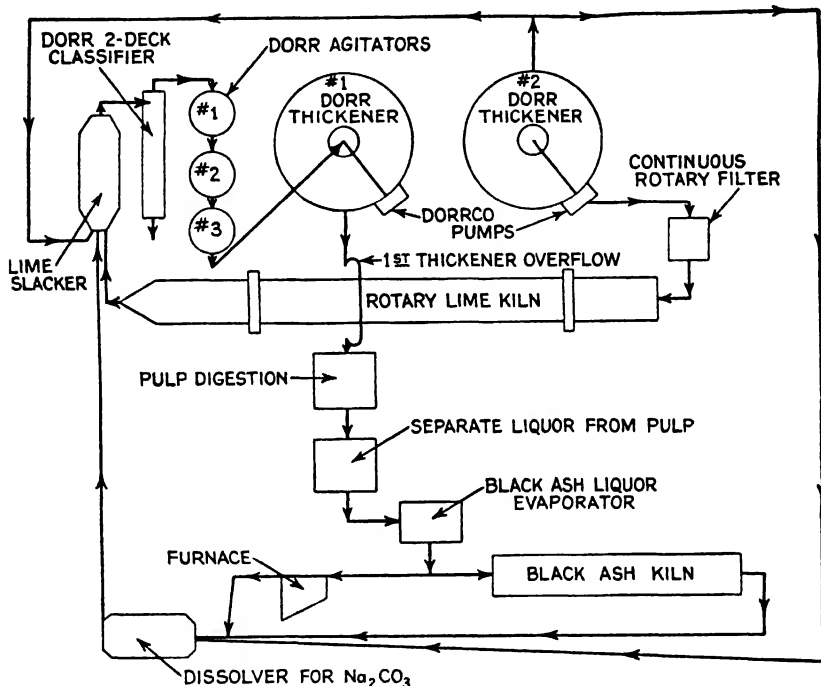


Fig. 77.—Recausticizing "Black Ash." Courtesy The Dorr Company, Inc., New York City.

equipped with stirrers, or in towers in which the soda solution containing lime in suspension is heated as it passes down against rising steam. In either case the precipitate is allowed to settle from the caustic solution. In the continuous process, soda ash (or crude sodium carbonate from recovery operations) is ground wet with lump lime in closed circuit with a classifier. The resulting suspension passes through a series of heated reaction agitators, and thence to a series of thickeners. By employing counter-current methods, the overflow from the thickeners is around 10% caustic soda concentration, which is suffi-

cient to be used in the soda process for paper pulp. The mud that is discharged has at the same time been washed practically free from sodium hydroxide. Solid caustic soda results from evaporation, insoluble substances being settled out during the process. When the concentration of caustic soda has reached its limit of efficiency in ordinary steam-heated evaporators, it is sent to open iron pots heated by direct fire. The chief difficulty in evaporating caustic soda solutions is the embrittlement of steel. Cast iron is affected and may be used only in evaporator shells, and not in the sheets and tubes. A special evaporator has been developed in which all heating surfaces are of nickel. By the use of forced circulation, comparatively small vertical steam chests are adequate. In such an evaporator functioning with a single effect, concentrations of 70% are said to be possible. The final product from the pots is a fused caustic, which is either cast in steel drums, cooled, and ground to a powder, or formed into flakes by chilling a thin layer of the fused material on a polished steel drum and scraping it off.

Sodium hydroxide is sold on the basis of sodium oxide content (Na_2O) as 74%, 76%, and 78%. This refers to sodium hydroxide of 94.4%, 96.9%, and 98.7% purity. The remainder is moisture and small amounts of sodium carbonate, sodium sulfate, and sodium chloride. The distribution of the sodium hydroxide in the United States in 1929, 1930, and 1931 as given by *Chemical and Metallurgical Engineering* was:

USES	1000 TONS		
	1929	1930	1931
Petroleum refining	134	117	100
Rayon	111	110	110
Soap	108	100	95
Chemicals	135	117	100
Exports	60	63	66*
Textiles	42	30	32
Rubber reclaiming	40	20	14
Pulp and paper	45	42	37
Lye	25	22	18
Vegetable oil refining	11	10	9
Miscellaneous	48	38	34
	659	652	605

SODIUM SULFATE

Sodium sulfate in the form of the decahydrate occurs in deposits of considerable size, but for the most part they are in regions too remote to make this a profitable source. It is calcined before being shipped. Sodium sulfate is primarily a by-product from the manufacture of nitric and hydrochloric acids. The material from the sodium nitrate-sulfuric acid process for nitric acid is known as "niter cake." This material is either a mixture of neutral and acid sodium sulfates, or is more commonly the acid sulfate containing from 3% to 5% free acid. This is added to salt in a furnace to produce hydrogen chloride, which is absorbed in water to form hydrochloric acid. At one time the demand for hydrochloric acid was not sufficient to assimilate all this material. Owing to the greatly increased production of nitric acid during the war period, vast amounts of niter cake accumulated. In the course of time the excess was absorbed. The use of nitric oxide from ammonia oxidation for nitric acid manufacture has changed the situation very markedly, and it is likely that sodium sulfate will have to be made to a considerable extent directly from salt and sulfuric acid.

Sodium sulfate is used very extensively in the glass industry and is an ingredient of most dye baths. Sodium sulfide is made by heating the sulfate with carbon in a rotary furnace. The "sulfate" process for the production of wood pulp is essentially a digestion of the chips with a solution containing sodium sulfide and sodium hydroxide. The liquor that is drawn from the cooked chips is evaporated and calcined with the addition of sodium sulfate.

SODIUM SILICATE

Solutions of sodium silicate are known as "water glass." This substance is made in furnaces, which are essentially glass tanks, by fusing together sand, soda, and charcoal for several hours. The molten material may be cooled and ground, but it is more conveniently disintegrated by running it into slowly rotating cylinders partially filled with water. Sodium silicate solutions are produced by heating the coarsely powdered salt in water under steam pressure. Sodium silicate as it appears on the market contains considerably more silica than is represented by the formula $\text{Na}_2\text{O} \cdot \text{SiO}_2$, or Na_2SiO_3 . When sodium silicate is treated in solution with an acid, silicic acid results. This is in turn dehydrated to form a very porous and highly adsorbing material called "silica gel." Sodium silicate is used as an adhesive in

making paper boxes and similar containers, as a bonding material for abrasive wheels, and as an acid-proof cement, as a fireproofing material for textiles, and as a filler for soap. Eggs may be preserved by covering them with a solution of sodium silicate.

(Sodium nitrate has already been discussed in connection with nitrogen compounds.)

POTASSIUM COMPOUNDS

Since the chief use of potassium compounds produced by industrial processes is as a plant food, these compounds are discussed in the chapter on Mixed Fertilizers.

CALCIUM CARBONATE

Marble is a very hard and quite pure crystalline form of calcium carbonate. Transparent crystals are found in small amounts as calcite and aragonite. Limestones of various sorts are made up largely of calcium carbonate. Marls are deposits of calcium carbonate that are the results of solution of limestone in water containing carbonic acid and subsequent precipitation. Dolomite is a mixture of calcium and magnesium carbonates. Calcium carbonate is extensively used in the chemical industry as a neutralizing agent. Large quantities result as a by-product in many industries. Very pure and finely divided calcium carbonate has a limited use, and is made by the action of carbon dioxide on a suspension of calcium hydroxide.

CALCIUM OXIDE

The term "lime" is applied rather indiscriminately to calcium oxide, CaO , and calcium hydroxide, Ca(OH)_2 . The two are distinguished from each other by calling calcium oxide "quicklime" and calcium hydroxide "hydrated" or "slaked lime." Commercial lime may contain considerable amounts of magnesium oxide and still be known as "lime," since the physical and chemical properties of the two are similar. Lime containing more than 5% magnesia is called "magnesium lime," and the product of the calcination of dolomite is known as "dolomitic" or "high-magnesium lime."

Commercial quicklime is made by heating limestone, the equilibrium being $\text{CaCO}_3 + 42,500 \text{ calories} \rightleftharpoons \text{CaO} + \text{CO}_2$. The vapor pressure of carbon dioxide is appreciable at 700°C . and at 900°C . is around 700 mm. No temperature attained at any point in a lime kiln is sufficient to melt pure calcium oxide, but ordinary limestone contains

enough silica, alumina, ferric oxide, and alkalis to make possible a

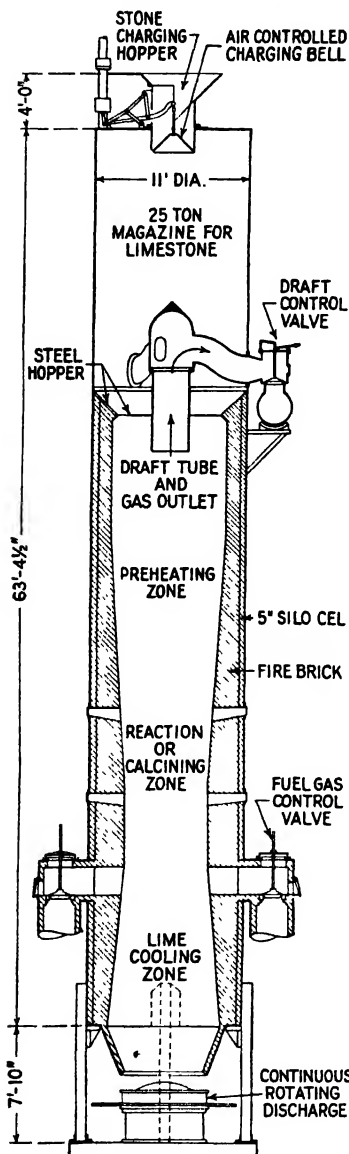


FIG. 78.—Mount Continuous Discharge Gas-Fired Kiln Courtesy Mr. W. D. Mount, Lynchburg, Va.

heated by burning producer gas. The finished product is cooled by

fused layer on the surface of lumps of quicklime unless the temperature is controlled. This serves to retard and render incomplete the decomposition of carbonates, and to interfere seriously with the slaking of the product. Magnesium oxide is not considered an impurity in building limes, high-magnesia limes being essentially the same for construction purposes as a high-calcium lime. High-magnesium limes can be used in the chemical industry for only a few special purposes, as for example in making bisulfite liquor, where the magnesium content is desirable. In some cases, magnesium merely dilutes the material, and this lowers its value; and in others, it is positively objectionable, as in the Solvay process for the recovery of ammonia, and in the beet sugar industry. If silica, alumina, and iron are excessive, that is above 5%, the slaked product is not sufficiently plastic for use in building operations.

Rotary kilns are used for finely divided calcium carbonate for materials such as fines from breakers, wastes from causticizing sodium carbonate and similar operations, for dolomite, and for magnesite, and are continually increasing in their use. A vertical kiln is a steel cylinder lined with firebrick with a vertical height up to 75 ft. and a diameter up to 10 ft. The material to be calcined is fed in the form of lumps at the top, is preheated by the waste gases, and finally

air admitted at the bottom of the kiln, and is discharged at intervals at the same rate as the kiln is fed. A part of the stack gas passes through the grate bars of the producer, thus furnishing carbon dioxide for reduction to carbon monoxide without developing excessive temperatures in the combustion zone.

Quicklime varies in color from white to gray, and is somewhat lower in specific gravity and more porous than the rock from which it was formed. It is used without slaking for a few purposes such as drying gases, producing absolute alcohol, and in the calcium saccharate process for recovering sugar from beet molasses, but for many purposes is slaked before it is finally used. Since slaking means the addition of 18 lb. of water to every 56 lb. of quicklime, slaking is often not done until the lime is ready to be used, thus avoiding shipping costs.

CALCIUM HYDROXIDE

When water is brought in contact with calcium oxide the following reaction takes place, which is known as slaking:



If slaking is carried out with large masses in a closed space, the temperature attained may reach 400° C. During the slaking operation there is an increase in bulk of around three fold. Air slaking results mainly in disintegrating lump lime to a powder, converting it to calcium hydroxide, and increasing its weight and bulk, rather than returning it to the form of carbonate.

Where only small amounts are wanted at any one time, quicklime and water are mixed and stirred with a hoe in shallow wooden boxes to form a thick paste. A dry powder is made in large-scale operations by mixing finely ground quicklime and water in about theoretical proportions either in revolving pans equipped with stationary stirrers, or in a continuous hydrator in which the material is passed from one shelf or tray to another by means of revolving rakes, steam being condensed and the water returned. The product is again screened and the oversize is ground.

Slaked lime is widely used in chemical industries, about 50% of all this material made in the United States finding use in such ways as causticization of sodium carbonate, ammonia production, water treatment, glass making, and wherever a cheap alkaline substance is needed and calcium salts are not objectionable. Agriculture absorbs about 12% of lime in the treatment of acid or plastic clay soils. Slaked

lime is used in the building industry as a plasticizer and tightener for concrete, as a wall plaster, and as a component of mortar.

There is very little experimental evidence as to the way in which lime mortar sets. It is rather generally agreed that the initial hardening is solely a matter of drying. Since the lime is largely in the colloidal state, it hardens like a glue and binds together the sand grains. This initial setting gives the mortar sufficient strength for ordinary walls. It is probable that minute crystals of calcium hydroxide form after the mortar has stood for some time. When the moisture content has dropped to a value of the order of 7%, carbon dioxide of the air begins to react with calcium hydroxide to form calcium carbonate. This is regarded as a second setting process. The reaction is a very slow one, the penetration for the first year being of the order of 0.1 in. The sand grains serve to permit more ready access of carbon dioxide to the interior of the mass. Mortars in the interior of very thick walls, which have been examined after standing for centuries, still contain free lime. If considerable weight is to be carried by the wall and construction must be rapid, portland cement is incorporated in the mortar.

CALCIUM SULFATE

Calcium sulfate occurs in all degrees of purity, the purest variety being alabaster. It may also occur in transparent crystals known as "selenite" and in long needles as "satin spar." Rock gypsum and gypsum sand may be quite pure, but many deposits are contaminated with silica, ferric oxide, and alumina. Gypsite is a crude material containing not more than 50% calcium sulfate. A great deal of naturally occurring calcium sulfate is in the form of the hydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, known as gypsum. Anhydrite is calcium sulfate without water of hydration, and is also quite abundant. Calcium sulfate deposits are very extensive in the United States, being very widely distributed over the western half of the country.

The purest material is used in making what is known as "plaster of paris"; lower grades produce ordinary wall plaster and wall board. The principle involved in their manufacture and use is the same. When gypsum is heated to a temperature of about 170°C . the dihydrate loses water to give a lower hydrate, the equilibrium shifting practically completely to the right:



When the lower hemihydrate is brought in contact with water at

ordinary temperature it takes up three mols of water to form two mols of gypsum. During this process of hydration, the mixture becomes quite plastic, and can be easily worked into the desired form. This reaction is quite rapid, and must be retarded by colloidal material in the making of casts and the application of wall plaster. This is accomplished by mixing a cheap lime soap with the hemihydrate. Dental molds made of plaster of paris are caused to harden rapidly by addition of sodium chloride as an accelerator.

The conversion of the dihydrate to the hemihydrate is accomplished commercially by two general methods. In one the finely ground gypsum is handled in a "kettle" or vertical cylinder with a concave bottom, equipped with a powerful stirrer, curved to conform to the bottom of the kettle. In a kettle of 8 ft. to 10 ft. in diameter, the center of the bottom is about 1 ft. higher than the edges. Direct heat from a fire reaches the bottom while the hot gases pass up around the walls. The kettles are made in sections, so that the bottoms, which burn out easily, may be replaced. Flues through the kettles may also be provided to increase the heating surface. From 7 to 12 tons are used at a single run. Any water not in chemical combination passes off at its boiling point with consequent agitation of the powder to give the appearance of boiling. When the transition temperature of the dihydrate is reached, water escapes and the contents of the kettle again appear to be boiling. The temperature is carefully watched and held below 170°C . except in the case of lower-grade materials, where it may rise to 200°C . At the end of the operation the contents of the kettle are run from a door in the side of the kettle near the bottom into a fire-proof pit, and after cooling are screened and packaged.

The second process includes heating coarsely ground and dried rock gypsum in rotating kilns, which are both externally and internally heated by furnace gases, and discharging the hot and partially dehydrated material into concrete bins lined with firebrick. A part of the water is removed in the kiln, and the remainder escapes from the stored material, leaving hemihydrate. When calcination is complete, the product is cooled rapidly by passing air through it, and is then ground and screened. This process may be carried out continuously by proper rotation in the order of bins.

If the heating of gypsum is carried out at a red heat, an anhydrous material results that takes up water very slowly indeed. However, there are always a few crystals that serve as nuclei to start the formation of the dihydrate. A hard finish plaster is made by heating gypsum by direct contact with furnace gases to 500°C . until all but a trace of

water is removed. What is known as "Keene's Cement" is made by burning the gypsum at red heat, cooling it, impregnating it with solutions of alum, and heating it again at a high temperature. The finely ground product mixed with water sets to a very hard substance and is used for door facings, window sills, and floors. The bulk of calcined gypsum is used as a plaster, in wall board, and in insulating materials of building construction. Calcium sulfate is a minor ingredient of portland cement.

MAGNESIUM COMPOUNDS

Magnesium compounds other than silicates are found in commercially important quantities and in usable form as magnesium carbonate and magnesium chloride. Magnesite is practically completely composed of magnesium carbonate. Dolomite is a mixture of approximately equivalent amounts of magnesium and calcium carbonates. A dolomitic limestone contains much less magnesium than calcium. Magnesium chloride is found largely in salt deposits and in brines.

Magnesium oxide, MgO , or magnesite is made by calcining magnesite at 1700°C . It is used largely as a refractory, having an incipient fusion point at 1800°C . to 2000°C . It has a heat conductivity about three times that of silica brick. The product of proper calcination is quite dense and does not easily recarbonate on exposure to moisture and carbon dioxide.

A basic magnesium carbonate of approximately the formula $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ finds extensive use as the main ingredient in molded steam-pipe coverings. Asbestos fiber serves to give the material mechanical strength. Dolomite is calcined with coke, and the carbon dioxide from the kilns is used to precipitate calcium carbonate from a suspension of the slaked material. The filtrate, a magnesium bicarbonate solution, is boiled, and the basic carbonate precipitates.

Magnesium chloride and magnesium oxide are both used as a source of metallic magnesium. Magnesium chloride finds its chief use as a cement along with magnesium oxide, the material being known as magnesium oxychloride, the crystalline product corresponding roughly to three mols of hydroxide per mol of chloride and seven mols of water. It serves as a binder for powdered rock, ground cork, and sawdust, the material showing considerable mechanical strength. With fibrous materials it produces resilient and permanent floors.

CHAPTER XV

MIXED FERTILIZERS

A fertilizer in agriculture refers to a substance containing elements essential to plant growth that are not supplied by natural means fast enough to keep up with the rate of removal of those elements by drainage and by crops. The three principal essential elements whose compounds appear in mixed fertilizers are nitrogen, phosphorus, and potassium. The general practice in the United States is to add those elements which a particular soil requires for the growing of a certain crop in the form of a mixture of the compounds just referred to, together with a very considerable amount of natural carriers with which the essential elements are chemically combined, and some inert impurities. Several other elements are essential and often have to be supplied. Chief among these is sulfur, and this deficiency may be supplied by the use of ground brimstone, calcium sulfate, and magnesium sulfate. Magnesium and sulfur are both added by the last-named compound, but the magnesium may be supplied by ground dolomite. Other elements of importance are manganese, copper, and iodine. The amounts of these elements necessary to maintain proper soil conditions are small, and were probably once supplied by the older types of fertilizer such as barnyard manure. Their lack became noticeable when the newer synthetic materials of higher nitrogen, phosphorus, and potash content began to be used. The special requirements of each soil are determined and deficiencies supplied primarily by the use of mixed fertilizers containing the three common elements just mentioned; minor deficiencies are taken care of by the necessary compounds of the missing elements in the form of relatively pure substances.

The terms used in evaluating fertilizers are the result of long custom. A commercial fertilizer labeled 3 : 10 : 4 means that it contains nitrogen, phosphorus, and potassium in the following proportions:

Nitrogen, 3%. Until recent years nitrogen was always reported and referred to in terms of ammonia, and this system is still used to some extent.

Phosphorus as phosphorus pentoxide, P_2O_5 , 10%.

Potassium as potassium oxide, K_2O , 4%.

Phosphorus pentoxide is referred to in the fertilizer trade as "phosphoric acid." The term "bone phosphate of lime" (B.P.L.) refers to tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, and usually applies to the evaluation both of bones and of phosphate rock. The remainder of the fertilizer, largely the natural carriers of the essential elements, is inert matter. Material known as a "conditioner" commonly counteracts the tendency of hygroscopic materials to cake. Fibrous materials of low specific gravity are quite popular. Some of these are themselves low-grade fertilizers. It would be a great saving in transportation costs if the concentrated materials were bought in bulk and weighed and mixed on the farm, but so far few agricultural enterprises are sufficiently large to make such practice feasible.

The price of a fertilizer is determined by the amount of each of its three essential components. One per cent is called a "unit," which amounts to 20 lb. per short ton, and prices are commonly quoted on the costs of a unit of nitrogen or ammonia, phosphoric acid, and potassium oxide.

It would appear that a limited number of mixtures would meet all possible needs, and various agricultural conferences have recommended that all fertilizers be restricted to certain combinations for each district in the United States. There is an increasing tendency on the part of agriculturists to use more concentrated fertilizers. As an example, a 10 : 16 : 14 mixture is now being used where formerly the accepted material was 5 : 8 : 7.

Any data regarding fertilizers later than 1929 are apt to be somewhat misleading because of abnormal business conditions throughout the world. A few facts are given here to indicate the magnitude of this industry in the United States and in the world.

In 1928 the world consumption of fertilizers was of the order of 7,700,000 tons of plant foods in terms of nitrogen, phosphoric acid, and potassium oxide. Following are the nations consuming more than 100,000 tons of combined plant foods.

COUNTRIES	1000 TONS	COUNTRIES	1000 TONS
Germany	1834	Great Britain (with North Ireland).	274
United States (with Puerto Rico and Hawaii).	1488	Spain	270
France.	953	Poland.	232
Japan.	420	Belgium.	153
Italy.	339	Czechoslovakia	153
Netherlands.	322	Australia	132

Of these plant foods the distribution is estimated as follows:

Nitrogen (N).....	1,901,000 tons
Phosphoric Acid (P_2O_5).....	3,736,000 tons
Potash (K_2O).....	2,025,500 tons

These plant foods were contained in about 43,000,000 tons of various fertilizer materials.

NITROGEN COMPOUNDS

The nitrogen compounds in fertilizers may be regarded as falling in these three classes:

1. Nitrates, which are immediately used by the plant.
2. Ammonium compounds, which are more slowly available, and are largely oxidized to nitrates in the soil.
3. Organic nitrogen compounds, which are protein materials and calcium cyanamid, which require considerable time for conversion to ammonium compounds, and thence to nitrates. Calcium cyanamid refers in the fertilizer industry to the "lime-nitrogen" product obtained by the action of nitrogen on calcium carbide, after this material has been treated with water to decompose carbides and to hydrate free lime and has been oiled to keep down dust. Its chief component is the calcium derivative of cyanamide, and it contains from 22% to 23% nitrogen. In the soil it is said to form urea, which functions like ammonium compounds.

The production of the more important nitrogen compounds used as fertilizers is discussed in the chapter on Fixed Nitrogen. It is only necessary to enumerate very briefly some of the sources of nitrogen other than ammonium salts and nitrates. These are mainly from organic wastes. This type of material will always have a limited use, but the bulk of nitrogen from plant foods will increasingly come from the synthetic chemical industry. Probably not more than 10% of the fixed nitrogen for fertilizers used in the United States is from organic wastes. These sources are mainly as follows:

- Farm manure. (Since this material has only local use and is not an industrial product, it has little bearing on the production and sale of fertilizer.)
- Hoof meal.
- Hair and wool waste, and leather scrap (usually processed and rendered available before being applied to the soil).
- Castor pomace (unfit for animal food).
- Fish scrap.
- Dried blood.

Garbage tankage (dried solids plus solids resulting from evaporating liquids from which grease has been removed).

Sewage sludge.

Guano (a limited amount from bat caves; mainly from rainless islands of South American Coast).

Base goods (a term applied to all sorts of waste material containing nitrogen).

Packing-house tankage (dried scrap and solids from degreased and evaporated liquids; also used as cattle feed).

Cottonseed meal. (Although the largest use of this substance is as a stock feed, it is also the most widely used in the fertilizer field of all organic by-products.)

POTASSIUM COMPOUNDS

An estimate of the elements that go to make up the earth's crust indicates that potassium is slightly more abundant than sodium. However, in compounds that are soluble, sodium occurs in vastly greater quantities than potassium. In the soil, potassium is present in the form of complex silicates. Solutions of calcium and magnesium salts react with these silicates with an exchange of bases much after the fashion in which water is softened by the zeolite process. Potassium compounds are thus very slowly made available to plants. In order to supplement this source, potassium salts are used in practically all mixed fertilizers.

The chief source of the world's supply of potash is in two countries in Europe: Germany and France. The first deposits to be developed in Germany are in the vicinity of Stassfurt, and underlie an area of 100 square miles. There are other extensive deposits in Germany. It is estimated that the German deposits represent eleven billion cubic meters, and are sufficient to supply the world's markets at the present rate of consumption for a period of ten centuries. In the German deposits the types of minerals from which potassium salts may be obtained are: carnallite, $\text{MgCl}_2 \cdot \text{KCl} \cdot 6 \text{H}_2\text{O}$; polyhalite, $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2 \text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$; and sylvinite, a double chloride of sodium and potassium of varying composition. Associated with them in these deposits are rock salt, gypsum, kieserite, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, and sandstone. The average content of the material mined is around 12% in terms of potassium oxide. The salts are obtained by sinking shafts to the deposit and sending out galleries as far as it is profitable to go from the central shaft. The products obtained vary from a crude potassium chloride containing not more than 12% of this substance up to a 98% product. By-products of the industry are sodium chloride, sodium

sulfate, magnesium sulfate, magnesium chloride, bromides, borates, and rubidium compounds. The general principle of the process most commonly used is to dissolve the material as mined in a boiling saturated solution of magnesium and sodium chlorides, and to evaporate to a density of 32° Bé. The potassium chloride dissolves readily, but neither sodium chloride nor magnesium sulfate goes into solution to an appreciable extent. From this solution a product crystallizes, which contains around 64% potassium chloride. The mother liquor is concentrated under reduced pressure, and from it is recovered a double chloride of potassium and sodium resembling carnallite, which is added to the crude material from the mine. More concentrated products are made by fractional crystallization.

The production of potash salts of all kinds from German deposits in the last normal year before the World War was of the order of 1.11 million metric tons. This figure was not reached again until 1922, when the production was 1.35 million metric tons.

The deposits in Alsace between Colmar and Mühlhouse near the eastern slopes of Vosges Mountains are by no means so extensive as those in Germany, the amount being estimated at 190 million cubic meters. Although the deposits extend over an area of 65 square miles, they are in relatively thin layers. Very small amounts of sulfate are present, the salts being mainly chlorides.

American Potash. During the period of the World War the United States was cut off entirely from German potash. By virtue of excessive prices it was possible to utilize a number of sources of potash that could not be economically used with prices at normal levels. Even under the stimulus of high prices the maximum produced in a single year was less than one-fourth the amount usually imported by this country. During the war period the potash industry in the United States was a makeshift affair. The point of view was largely to make as much money as possible before the re-entrance of European potash, and to spend as little as possible on fundamental research. At present the United States uses 12% of all European production and 32% of all their exports. In 1928 the imports of potash in terms of potassium oxide were 297,000 tons, the total material containing this amount of potash being nearly one million tons. The total production of the United States was 59,910 tons of potassium oxide in 104,130 tons of material. The sources which were drawn upon during the war period were: alcohol and sugar residues, blast furnace and cement kiln dusts, silicates, alunite and kelp.

Potash Salt Deposits. In recent years considerable exploration has

been carried on in Texas and New Mexico to determine the extent of potassium salt deposits in that region. Very large amounts are indicated, and it is quite likely that these deposits will have a very considerable effect on the present potash situation in the United States. "Manure salts" of 25% to 28% potash content are now being mined in New Mexico. Production of the order of 500 tons per day was reported in the summer of 1932, the raw material being sylvinite. A substantial portion of the potash of this grade now being used in the Central, Southern, and Gulf States of the United States is from this source. A plant to refine these salts to a 60% K_2O content was reported as being built in 1932.

Brines. Several brine lakes in Nebraska were found to contain sufficient quantities of potassium salts to make extraction profitable at war prices. The total amount of potash was small, the engineering was hasty and crude, and all plants shut down shortly after the close of the war. The only producer of potash on large scale to survive the return of prices to a normal basis is a company operating at Searles Lake in California.

Searles Lake is now the main large-scale source of potassium salts in this country. This formation was at one time one of a series of connecting lakes. The elevation is around 1600 ft. above sea-level. What now remains of Searles Lake is a bed of salts from 11 to 12 square miles in area and from 50 to 125 ft. in depth, these salts being impregnated with a brine, which sometimes rises slightly above the surface according to the amount of rainfall or evaporation. Below the solids are several hundred feet of a mud composed largely of calcium sulfate and calcium and magnesium carbonates. The main salts of the deposit are: halite, $NaCl$; trona, $Na_2CO_3 \cdot NaHCO_3 \cdot 2 H_2O$; hanksite, $9 Na_2SO_4 \cdot 2 Na_2CO_3 \cdot KCl$; borax, $Na_2B_4O_7 \cdot 10 H_2O$; and glaserite, $3 K_2SO_4 \cdot Na_2SO_4$. The upper strata of the salt bed or the upper 15 ft. are made up mainly of sodium chloride. The composition of the brine in contact with these salts may be expressed in terms of six ions: sodium, potassium, chloride, carbonate, sulfate, and borate. There are small amounts of lithium, phosphate, and sulfide ions, and traces of calcium, ferrous iron, ammonia, antimony, arsenic, and iodine. The brine is of the order of 35% dissolved material, and of this potassium chloride represents about one-eighth. It is estimated that as much as 35,000,000 tons of potassium chloride can be obtained from Searles Lake. These salts have probably resulted from the leaching of soluble materials from neighboring volcanic mountains.

The first product obtained on a commercial scale from Searles Lake

was borax, but this industry later shifted to Death Valley. During the war period, under the stimulus of potash prices around ten times the normal figure, two plants produced a low grade of material containing borax as well as potash, which would have been entirely unsalable in competition with European potash.

At the close of the war period the price of potash dropped considerably below war levels. The one company which is now the only real factor in American potash production from brines sent the problem back into the laboratory, and made a very thorough and painstaking study of all the equilibria of the salts and brine. It was not merely a question of a two-component system, but of three-, four-, five-, and even six-component systems. The problem was infinitely more complex than that of European plants working with solid materials. After having worked out the equilibria, the chemists and engineers of the company found abundant difficulties in developing the commercial process. It would seem on the basis of superficial considerations that the low rainfall and low humidity and the long duration of very hot weather would have made solar evaporation the ideal system. Unfortunately the temperature undergoes very decided changes, and at some temperatures all salts separate together, and at others very unsatisfactory mixtures are obtained. For example, when evaporation takes place at 20° C. the complex salt separating first contains some potassium, but not enough for a marketable product. The quantity of potassium, however, is such that very little potash remains in solution when the limit of solubility of potassium chloride is reached.

Since the plant had been built and operated under conditions that did not require a high-grade product, the development could not follow the usual orthodox method of small-scale or pilot plant operation followed by design of the main plant. Changes had to be made as the plant ran, with gradual improvement to a satisfactory standard. Among some of the difficulties were: the formation of a scale of sodium-lithium-ammonium phosphate, which gave off ammonia and corroded the copper of the evaporators; excessive foaming; large quantities of non-condensable gases, mainly carbon dioxide from the decomposition of bicarbonates; and general lack of adaptability of the equipment to the process that the nature of the substances to be produced required. These difficulties were gradually overcome, and on the basis of this experience a new plant was built. The present plant is now producing both potassium chloride of 95% to 98% purity and a good grade of borax.

The brine is taken from a number of wells and is pumped to a one

million gallon reservoir. It is first evaporated in very large triple-effect evaporators equipped with a number of outside heaters. Fatty acid is used to prevent foaming. The sludge of burkeite, a double salt of the composition $\text{Na}_2\text{CO}_3 \cdot 2 \text{Na}_2\text{SO}_4$, and salt is removed, washed free of adhering liquor, and flushed back to the lake. The liquor from the third effect is saturated with respect to potassium chloride but not with borax. A little water is added to prevent any precipitation, and the hot liquor is passed through a series of continuous "flash coolers," in which a partial vacuum is maintained. Thus practically all the cooling is due to evaporation. Potassium chloride separates in a high degree of purity and is immediately removed in centrifugals. This product is dried by furnace gases in rotary drum dryers. The liquid separated from the potassium chloride is a supersaturated solution of borax. It is heated past the point of supersaturation and acidified sufficiently to insure conversion of metaborates to borax, and cooled in double-tube coolers to around 75°F . The solution then passes to vertical crystallizers, where it is thoroughly stirred and seeded with borax crystals. The crude borax that crystallizes is centrifuged, and the mother liquor is returned to the cycle. The borax from the centrifugals is recrystallized, again centrifuged, and carefully dried by steam-heated air in a double-walled rotary drum dryer to avoid loss of water of hydration from the crystals. In order to avoid accumulation of impurities, a part of the mother liquors from the recrystallization must be wasted.

The net result of the process is that the potash from this plant represents the bulk of the high-grade potash supply, as well as half of the borax supply, of this country.

PHOSPHORUS COMPOUNDS

The production of phosphorus and phosphoric acid by electric furnace methods is discussed in the chapter on Electrochemical Industries. So far this method of making phosphoric acid has little relation to the main use of phosphoric acid compounds as fertilizers. Some progress has been made towards the use of phosphoric acid as a carrier of ammonia instead of sulfuric acid. The obvious advantage is that both phosphorus and nitrogen are plant foods, whereas sulfates have somewhat less value for this purpose. Several concentrated mixed fertilizers are on the market containing sodium nitrate and disodium phosphate, and also mono-ammonium phosphate. Addition of potassium chloride and filler will give practically any desired formula. It

has been proposed to cheapen production costs of crude phosphoric acid by the use of coal-, oil-, or gas-fired furnaces for reducing low-grade phosphate rock, and this process has been worked on a commercial scale, one large blast furnace being in continuous operation. At present this phosphoric acid is used to make considerable amounts of "double superphosphate."

The main method of preparing phosphorus compounds for use as plant food is to treat crude calcium phosphate with moderately concentrated sulfuric acid. If inert material is not gotten rid of, the mixture is known as "superphosphate." At one time the term "acid phosphate" was used, but has recently been practically discarded. The elimination of varying amounts of calcium sulfate and of silicate materials results in products higher in phosphorus content, known as "double" or "treble superphosphates."

The compound that is the main constituent of phosphate rock is complex calcium fluoride-phosphate, and is so insoluble that it has practically no fertilizing value. In the presence of the decaying organic matter of ground, uncooked bone, it is slowly changed to compounds which the plant can use. Very large amounts of finely divided phosphate rock have undoubtedly increased crop yields, owing probably to slight action of carbonic acid. Pure tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, is quite insoluble, but is surprisingly "available" as a plant food.

Dicalcium phosphate, $\text{Ca}_2(\text{HPO}_4)_2$, is not soluble in water, but is sufficiently soluble in the soil solutions to be utilized by the plant, being adsorbed and converted by chemical action of plant juices into substances entering into the composition of the plant. It is known in industry as "reverted phosphoric acid."

Monocalcium phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, is soluble in water, and is immediately available to plants. However, since many soils are alkaline, very little of this material remains long in them in this form, being changed in the soil by reaction with the various bases present to compounds containing the HPO_4^- radical, a change known as "reversion." Hence both monocalcium and dicalcium phosphates are "available" as plant foods.

The value of a phosphate fertilizer cannot be determined wholly by chemical analysis, although this is the most common guide in judging such materials. The effect of other ingredients, the soil itself, and the degree of subdivision of the phosphate material, all have an influence on the value which it has as a plant food.

If crude phosphate rock and sulfuric acid of a sufficient dilution to

form hydrates with a part of the acid phosphates and with the calcium sulfate are mixed together, the resulting product, known as "superphosphate," will contain from 16% to 20% available phosphoric acid in terms of P_2O_5 . The materials are so proportioned as to yield mainly monocalcium phosphate together with a small amount of free phosphoric acid. The silicate materials of the rock and calcium sulfate remain in the product. The method of making acid phosphate is to run phosphate rock, ground largely to pass 100 mesh or finer, from a weighed hopper into a covered cast-iron pan containing 50° to 55° B \acute{e} sulfuric acid. The cover remains in position, but the pan revolves slowly, the contents being stirred by plows, which move at several times the speed of the pan. During the operation, gases continually escape, these being mainly carbon dioxide and silicon-fluorine compounds. Within two or three minutes the material is dropped into bins known as "dens." If allowed to remain longer in the mixing pan, the contents would set so that removal would be very difficult. The dens may be simple concrete bins from which the product, after solidification from 30 minutes to 24 hours, is removed by grab buckets or dug out by hand. More complex equipment is often used in which the dens have movable walls, and in which the block of acid phosphate is shaved off into conveyors.

To prepare a more concentrated material, dried phosphate rock is ground and treated with sufficient sulfuric acid to convert either the major portion of the phosphates or all of them to free phosphoric acid. The insoluble silicate residue and the precipitate of calcium sulfate are separated by filtration only, or by continuous counter-current decantation with the use of agitators and thickeners followed by continuous filters. The filtrate is concentrated and treated with enough ground phosphate rock to produce monocalcium phosphate as the main component.

Since this material and also mixed fertilizers are handled in burlap or cotton bags, it is necessary to protect the bags by neutralizing the free acid. The product is often left acid, and this is corrected before packing by the use of lime or calcium cyanamid. Such procedures result in a product ranging from 37% to 48% phosphoric acid (P_2O_5) content. In one large plant, 1.25 tons of 50° B \acute{e} sulfuric acid are used with each ton of phosphate rock, giving a product averaging 45% in terms of phosphorus pentoxide, and representing 85% of all phosphorus in the original rock. This very high-grade material is known as "double" or "treble superphosphate." There is no distinction between "double" and "treble superphosphate." At one time all material

made by the process described above was called "double superphosphate." Recently the term "treble" or "triple superphosphate" was coined in the United States to indicate a phosphate that contains about three times as much available phosphate as ordinary superphosphate. An ingenious method of correcting acidity in mixed fertilizers and at the same time of increasing nitrogen content is to sprinkle the material with anhydrous or aqua ammonia. In the 1929-1930 season some 30,000 tons of ammonia were used in this process of "ammoniation." When nitrates are used with superphosphates the free acid may liberate some nitric acid, and loss by volatilization of oxides of nitrogen may occur. Both ammonia and calcium cyanamid will neutralize free acid, prevent loss, and increase the nitrogen content.

Resources of phosphate rock in the United States are estimated to be around ten billion tons. These are found largely in the Rocky Mountain region, the South Atlantic States, and in Tennessee. There are large phosphate deposits in Northern Africa, in Russia, and on some of the islands of the Pacific and Indian Oceans, but the largest deposits are in this country. Only higher-grade rocks are ordinarily used, and fines are often wasted, only pebbles and clean lumps of rock being dried and ground at the plant. In recent years, however, there is a growing tendency to save even colloidal slimes. Phosphate rock occurs largely in the form of rock and pebbles. Rock phosphate will run from 50% to 80% calcium phosphate, the better grade of hard rock averaging around 77%. Land pebble usually contains 70% to 77% calcium phosphate. Ordinary quarry methods are used for hard rock. In some localities the rock is quite soft and may be mined by stripping the overburden of soil and taking it out with steam shovels. This material has the great disadvantage of containing excessive clay. Pebble phosphate is gotten by stripping off the overburden, hydraulic mining of the rock, washing off the adhering clay and sand, and drying.

Iron ores high in phosphorus are not so common in the United States as in Europe. The slag from basic Bessemer converters in which pig iron has been made into steel contains both tetraphosphates and double phosphate-silicates, which in finely divided condition have some fertilizer value. Some slag from basic open-hearth furnaces finds its way into fertilizer. Basic slag is a minor source of phosphorus compounds in this country, but is very important in Europe. It is estimated that, of the phosphorus compounds used in the entire world in fertilizer materials, superphosphates represent 69%, basic slag 26%, and other materials 5%.

Raw bones may be ground and this material used directly in mixed fertilizers, but it is better to steam the bones in order to extract the gelatin and grease. The steamed bone still contains some organic matter containing nitrogen. Both phosphorus and nitrogen from bone meal become slowly available by processes of decay in the soil. Spent boneblack from sugar refineries is used in much the same way as bone meal. Weathered guano contains very little nitrogen, its chief value being its calcium phosphate and its conferring certain desirable physical properties on mixed fertilizers, being known as a "conditioner."

CHAPTER XVI

HYDROCHLORIC ACID

Sodium chloride is the cheapest and most abundant of naturally occurring chlorides and is thus the most common source of hydrochloric acid. Some progress has been made in burning hydrogen in an atmosphere of chlorine. There are also certain processes such as the chlorination of hydrocarbons in which hydrogen chloride is a by-product. During the period of abnormally high nitric acid production (1914–1919), great quantities of niter cake accumulated, and much of this was used with salt to make hydrochloric acid. With the development of the ammonia oxidation process for nitric oxide, which in turn is converted to nitric acid, niter cake ceased to be abundant and is partially supplanted by sulfuric acid.

The oldest process for making hydrogen chloride was in "salt cake" furnaces. Sodium chloride and sulfuric acid were mixed in proportions to yield a residue of sodium sulfate, and the first step, the formation of sodium hydrogen sulfate with half of the salt unchanged, was carried out in a shallow, covered pan heated by furnace gases. The gas that was rich in hydrogen chloride was kept separate in its own absorption system. The molten material from the pan was raked over into a muffle furnace and heated by gases from a firebox, with continuous stirring with hand-operated rakes until conversion was complete. The muffle or "roaster" hydrogen chloride was very much diluted with the furnace gases and required a larger absorption system. This process flourished when the sodium sulfate was used in the Leblanc process for sodium carbonate, but has largely gone out of use.

The next process, and one which is still rather generally used, is a continuous one. A shallow, covered pan equipped with stirrers, which scrape over the bottom of the pan and are driven by a central shaft, receives sodium chloride near the center together with either sulfuric acid or molten niter cake. Hot gases from a firebox envelop the furnace. By the time the material has reached the periphery, the reaction is complete and sodium sulfate is discharged, while hydrogen chloride escapes and is conducted to the absorption system.

In recent years a continuous process was developed which used a sort of combination of rod mill and rotary kiln. The kiln portion was divided into a "grinding chamber" in which a cage of steel rails crushed and mixed the dry niter cake and salt as the whole cylinder turned, and a "hot chamber" through which the ground material passed, and in which most of the reaction took place. Burning gases

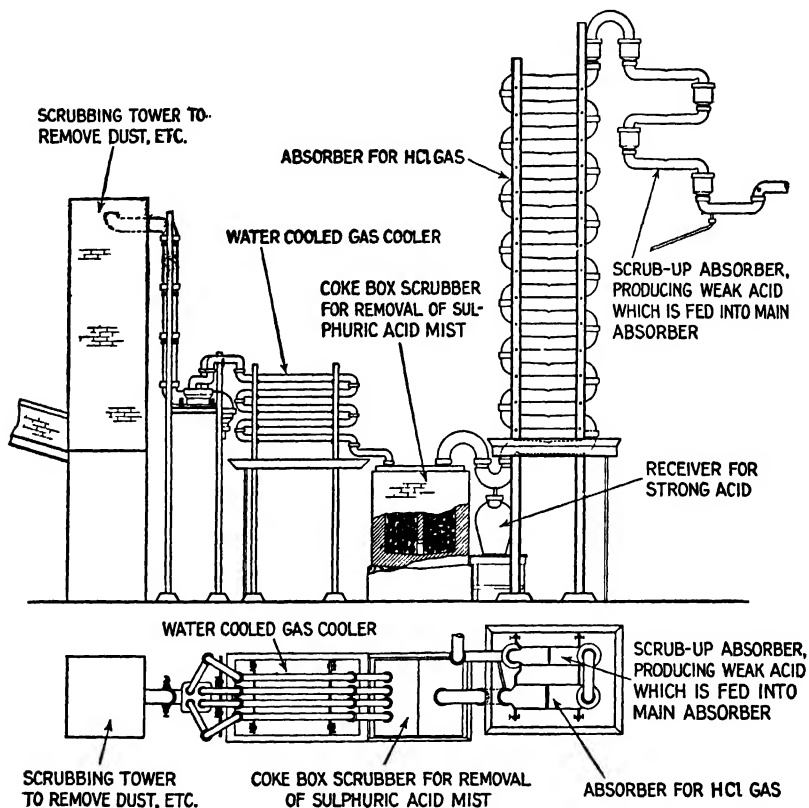


FIG. 79.—Tyler Hydrochloric Acid Absorption System. Courtesy The Thermal Syndicate, Ltd., Brooklyn, N. Y.

passed counter current to the feed. The ground material was discharged from the end next to the combustion chamber dry and practically free from chloride. This process depended on niter cake, of which comparatively small amounts are now made, but is being adapted to the use of sulfuric acid.

Hydrogen chloride is very soluble in water. In order to obtain concentrated solutions it is necessary to maintain as low a temperature

as possible, and to use a gas as rich as possible in hydrogen chloride. Considerable heat is developed during the solution of the gas, hence, in counter-current absorption, cooling the absorption system is essential. The rate of absorption is also cut down by exposing a limited water surface to the gas. When most of the hydrogen chloride has been taken up it is necessary to recirculate the dilute solution, and cooling is a minor consideration. The older method of preparing hydrochloric acid from gases carrying hydrogen chloride involved the use of large stoneware bottles of much the same type as the Woulfe bottle of the laboratory, and vessels of special shape, usually of U-shaped cross section, known as tourilles, through which the gases and absorbing liquids passed counter current. These were followed by packed towers equipped for recirculation. Fused silica S bends of slightly flattened silica tubing in which ridges insure a certain depth of absorbing liquid, and which the absorbing liquid passed downward counter current to the gases, constitute a very efficient system. The silica is relatively thin, has higher heat conductivity than stoneware, and is not affected by sudden temperature changes. In the section handling weak acid, short packed sections connect the horizontal absorbing tubes. A series of silica S bends, which are either air or water cooled, serve to lower the temperature of the gases before the absorption section is reached.

The bulk of hydrochloric acid used in industry is 20° Bé in specific gravity and contains 31.5% by weight of hydrogen chloride. Not much more than 10% of the acid used is 18° Bé or 28% hydrogen chloride, and very little stronger than 22° Bé is on the market, this being mainly required in laboratory work as a reagent. Hydrochloric acid is handled in glass, stoneware, rubber, and acid-proof brick-lined and cement-lined vessels, and is not employed if another acid can be substituted. Its uses are very varied. Its total production in the United States is of the order of 225,000 tons in terms of 20° Bé material.

CHAPTER XVII

ELECTROCHEMICAL INDUSTRIES

This chapter will be limited to the production of electric current by chemical action and to the use of the electric current in causing chemical changes.

Electrical Units and Terms. Definitions of such electrical units as coulomb, ampere, faraday, volt, ohm, and kilowatt can be found in physics and physical chemistry textbooks. There are certain terms that should be explained at the beginning of this discussion of industrial electrochemistry. Various efficiency terms occur in the description of electrochemical operations. The ratio of the quantity of current theoretically necessary to that actually required, expressed as a percentage, is called *current efficiency*. It also may be said that the ratio of the amount of a substance actually produced to that theoretically possible from the use of a given quantity of current, expressed as a percentage, is *current efficiency*. Practically always, higher voltages than theoretical are necessary. The ratio of theoretical to actual voltage is the *voltage efficiency*. The product of this ratio and the current efficiency is the *energy efficiency*. This value may also be defined as the ratio of theoretical to actual energy. Data on energy efficiency are of little value unless based on long performance periods, in which temporary abnormal conditions can be adjusted.

Current density refers to the quantity of current that is supplied to a given area of electrode, and is in terms of amperes per square foot, or, where the metric system is in use, in amperes per square centimeter or decimeter, or current per unit of area.

There are also three terms used in connection with electrochemical industries that should be referred to briefly, although it is beyond the scope of this book to give a detailed explanation of them. These terms are "polarization," "overvoltage," and "passivity."

Polarization has been defined as a "counter electromotive force caused either by exhaustion of the substances used in the electrolytic reaction faster than they can be replaced, or by the accumulation of the products faster than they can be removed." Polarization that is

due to changes of concentration around the electrodes is referred to as "concentration polarization," and can be obviated by stirring. Non-conducting films, which partially or wholly prevent contact of the ions with an electrode, are causes of polarization effects. Any process by which substances that cause polarization are removed is called "depolarization."

Overvoltage refers to a deviation from the equilibrium potential; it is measured in terms of the difference between the voltage required to cause evolution of a gas such as hydrogen, oxygen, or chlorine and the equilibrium potential value of the gas in contact with the same electrolyte. For example, it requires more than a volt higher potential to liberate hydrogen from the surface of a mercury cathode than it does from the surface of platinum covered with colloidal "platinum black." The equilibrium potential of a hydrogen electrode is measured with such a platinized platinum surface as the inert conducting material. Overvoltages increase with increased current density, and the increase is greater than can be accounted for by changes in the concentration of the electrolyte. Overvoltage is an important consideration in many electrochemical operations, not only increasing power consumption, but also changing the whole nature of a process.

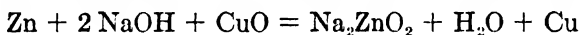
Passivity has been defined as "abnormal resistance to anodic solution." The phenomenon is observed in connection with the resistance of such metals as iron to the action of nitric and sulfuric acids. Chromium and nickel may also be gotten into the passive state. Passivity is often met with in connection with electrolytic cells, certain metals either failing to dissolve at all or dissolving in quantities much less than those corresponding to the current passed through the solution. Ions strongly oxidizing in their nature favor the passivation of metals like iron, whereas halogen ions retard the effect. Passivity increases with current density. It is closely associated with the evolution of oxygen and with active oxidizing agents, hence the formation of adsorbed oxygen compounds has been advanced as an explanation.

Chemical Action as a Source of Electric Current. In industrial practice only a very limited number of substances may be economically used to produce electric current by chemical action.

The term "cell" in its strictest sense refers to a positive and a negative electrode in contact with a solution containing electrolyte; a "battery" means a group of cells electrically connected. The term "primary cell" refers to those not practically and economically reversible. Such cells are used where relatively small quantities of current are needed intermittently and it is inconvenient or impossible to

employ a fixed source of current. There are, however, so many uses for primary cells that, from the standpoint of value, manufacture of such cells constitutes probably the largest of all electrochemical industries. "Secondary cells" are commonly known as storage batteries, and are cells in which the products of those chemical changes resulting in an electric current may be restored to their original condition by the use of an electric current. Such cells have a more diversified use than primary cells, not only meeting larger intermittent requirements, but also functioning as accumulators of surplus power when demands are light, and supplementary sources of current in times of peak loads.

Primary Cells. Practically all primary cells use zinc as the material of the anode. The familiar copper-zinc cell employing sulfuric acid and copper and zinc sulfate solution as the electrolyte now has only very limited use. A primary cell very extensively used has sodium hydroxide as the electrolyte, and zinc and compressed cupric oxide as electrodes. As zinc gives up electrons to the circuit and passes into solution it probably forms zincate ions, ZnO_2^- . The copper of the oxide is reduced to metallic copper. The copper oxide also functions as a depolarizer. The reaction may be considered to be



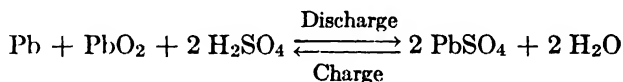
The electrodes may be cylindrical or in the form of plates, and the containing jar is made of glass. Activated carbon cathodes are now being used in an important type of cell with zinc as the material of the opposite electrodes and caustic soda as the electrolyte. The oxygen of the air adsorbed by the carbon acts as the depolarizing agent. Batteries of the type just described find very wide use, particularly in railway signal work. They range in size from 75 to 1000 ampere-hours rated capacity.

What is known as the "dry cell" is not dry, but the electrolyte is either in the form of a jelly made by gelatin, starch, or similar colloidal materials, or more commonly is held in an absorbent material. The zinc electrode is itself the container of the cell, being insulated on the outside by paper or pasteboard. The electrolyte is a solution of zinc chloride and ammonium chloride. The second electrode is a carbon rod surrounded by granular manganese dioxide as a depolarizer. The conductivity of the manganese dioxide is increased by the addition of graphite. This mixture very nearly fills the cell, and is either contained in cloth or pulp board. The cell is commonly sealed at the top by a wax, through which the terminals project, but in some cells a vent is left for the escape of gas. As the current flows, zinc dissolves

and goes into solution in the form of the complex zinc ammonia ion $\text{Zn}(\text{NH}_3)_4^{++}$. Hydrogen is liberated and reduces the manganese dioxide to form the compound Mn_2O_3 . As the cell is used, zinc dissolves and the manganese dioxide is reduced until no more current can be profitably obtained.

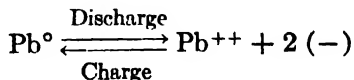
Secondary Cells. The most widely used secondary cell or storage battery is the lead-sulfuric acid type, but for certain purposes the nickel-iron-caustic cell is employed. Small portable lead-sulfuric acid batteries employ hard rubber containers for each cell, three or more of these cells being held in a wooden or soft rubber box. Larger stationary units are of glass or lead-lined wood. When the cell is fully charged, the electrolyte is dilute sulfuric acid of a maximum concentration of about 32%, corresponding to a specific gravity of 1.3. The electrodes are lead plates or grids separated from each other by insulators of thin wood or perforated rubber. When the cell is charged, the active material on the negative plate is spongy lead, and on the positive plate, lead dioxide, PbO_2 . The plates may be solid with their surfaces increased by means of stamped designs or cut furrows, or they may be grids in the openings of which the active materials are held. The latter type is known as a "pasted" plate.

The reaction usually accepted as most simply representing the chemical action of the lead-sulfuric acid storage battery is

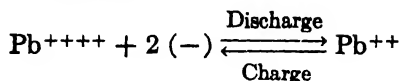


At the negative electrode, lead loses electrons as the cell discharges and the lead ions combine with sulfate ions to form lead sulfate. At the positive electrode, tetravalent lead is reduced by the stream of electrons to divalent lead, lead sulfate being formed as the lead dioxide disappears. As the battery discharges, the active material on both plates becomes lead sulfate. Sulfuric acid is used up, water forms, and the specific gravity of the electrolyte drops.

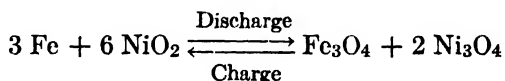
When charging takes place the lead ions at the negative electrode take up electrons, lead is deposited, and more lead sulfate dissolves to maintain the supply of lead ions. At the positive electrode, divalent lead loses two electrons and becomes tetravalent lead with the formation of lead dioxide. The reactions may be summed up as follows: At the negative electrode:



At the positive electrode:



The nickel-iron-caustic cell employs positive plates made of a series of perforated steel tubes clamped into a frame, the tubes being filled with an active material, which is regarded as being nickel peroxide, NiO_2 . Along with it is a little flake nickel. The negative plates are grids made up of nickel-plated and perforated steel boxes containing iron mixed with a little mercury. A nickel-plated steel can function as the container and is insulated from the plates by hard rubber sheets. Hard rubber pins hold positive and negative plates apart. The electrolyte is a 21% solution of potassium hydroxide containing small amounts of lithium hydroxide. The reactions of the cell are represented by Mantell as follows:



The oxides are probably hydrated.

Electrolysis from Aqueous Solutions. The passage of an electric current through aqueous solutions as a means of bringing about chemical change has many applications in industry. Among these the most important are the solution and deposition of metals, and the production of hydrogen, oxygen, chlorine, and caustic soda.

Electrowinning of Metals. The two metals in whose metallurgy electrochemical methods are of great importance are zinc and copper. *Zinc* of a high degree of purity is best obtained by electrowinning. From 25% to 30% of the zinc production in the United States is electrolytic. Zinc sulfate solutions result from leaching roasted concentrates with sulfuric acid and chemical removal of most of the accompanying elements. Electrolysis of zinc sulfate solutions containing sulfuric acid is carried out with insoluble anodes of lead or lead alloy, the zinc being deposited on cathodes of sheet aluminum. *Copper* can be profitably recovered from very low-grade ores by leaching methods followed by electrolytic deposition. In general, leaching is done by means of sulfuric acid containing ferric sulfate. The anodes used are either of lead alloyed with antimony, or a complex alloy composed mainly of copper, silicon, iron, and lead, while the cathodes are of copper. The yield of copper from hydrometallurgical processes

is from 80% to 90% of that shown by analysis to be present in the ore, and the product is slightly above 99% purity.

Electrorefining of Metals. The general procedure of electrorefining of metals is to employ anodes that are of a purity of from 95% to 99.5% in terms of the metal to be refined, to dissolve these anodes under the influence of the electric current, and to deposit the metal in a very high state of purity on cathodes of the pure metal or on cathodes of such nature that the deposit may be readily removed.

Copper. The important reasons for the electrolytic refining of copper are: increase in conductivity, improvement of rolling and

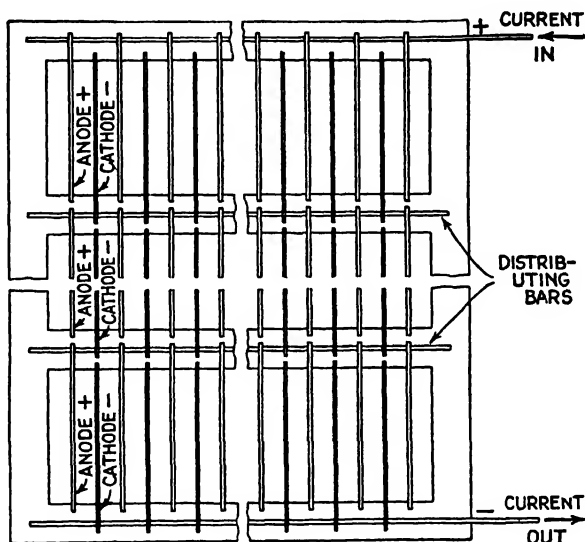


FIG. 80.—Plan of Nest of Tanks and Electrodes (Multiple System). Courtesy Raritan Copper Works, Perth Amboy, N. J.

drawing properties, and recovery of small amounts of gold and silver. Impurities soluble in the solid solution of copper have a marked influence upon the electrical conductivity of copper. One-tenth of one per cent of arsenic will lower the conductivity 25%, and a like amount of antimony 12%. Impurities insoluble in the solid solution, such as lead, bismuth, selenium, and tellurium, have little effect on conductivity but are extremely detrimental to the rolling and drawing properties of the metal. Both kinds of impurities must be reduced to a minimum; the sum total of the metallic impurities in refined copper is less than 100 parts per million (0.01%). The material to be refined varies in copper content from 99.0% to 99.5%. This material is commonly

"blister copper," whose production is described in the chapter on Metallurgy. It is melted in reverberatory furnaces and oxygen and sulfur largely removed with very little change in the amounts of other substances present. The product of these furnaces is cast into anodes which weigh from 500 to 770 lb. and are usually of the order of 3 ft. high and wide and slightly under 2 in. in thickness. They have projections or "lugs" at the top corners by which they are supported in the electrolyte, and which serve to make connections with the source of current.

The most common arrangement of electrodes in the refining of copper is known as the multiple system, in which all the crude copper

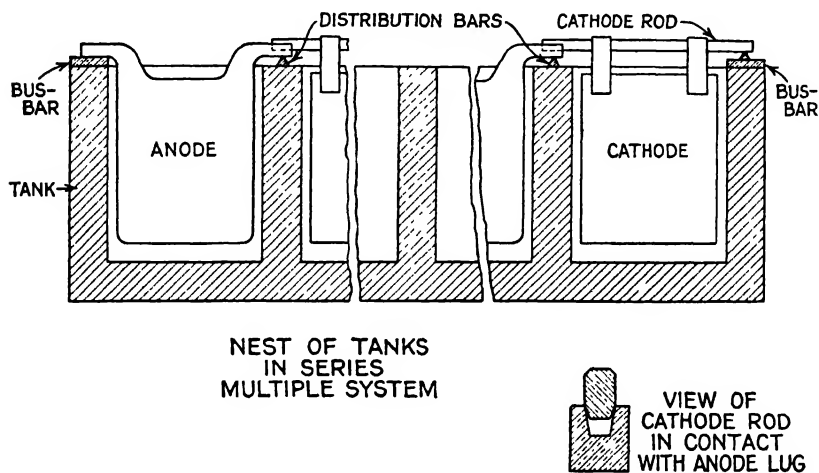


FIG. 81.—Cross Section of Nest of Tanks and Electrodes in Series (Multiple System). Courtesy Raritan Copper Works, Perth Amboy, N. J.

anodes in a single tank are connected to a common bus-bar; and in the same way all the cathodes, which are thin sheets of pure copper, are connected together. By employing distributing bars, two bus-bars can serve a series of parallel tanks. The series system, now practically obsolete, involves connecting only the two end electrodes. The intervening electrodes thus serve as bipolar electrodes, one side dissolving as anode and the other receiving deposits of pure metal as the cathode. By employing cathode bars of wedge-shaped cross section, cathodes in one tank may be connected to anodes in an adjoining tank, and contact resistance is thereby greatly reduced.

The electrolyte contains from 16% to 18% sulfuric acid and around

3% copper as copper sulfate. It is heated to 55°–60° C. before being run into the tanks, and is circulated by means of pumps or air lifts. Very small amounts of glue, mineral oil emulsions, or sulfonates are used to improve the deposit. Chloride ions to the extent of 20 to 30 parts per million assist in precipitating silver, bismuth, and antimony as insoluble chlorides. Usually two cathodes are made for each anode used, the life of an anode being from three to four weeks. When the anode has been dissolved to about one-tenth of its original weight, the remainder is removed as scrap and is reworked. Several hundred tanks are in operation at a time in a large refinery. Each tank has from 30 to 40 anodes and the corresponding number of cathodes. From 7000 to 10,000 amperes pass through each tank, the voltage is from 0.20 to 0.25 volt per tank, and the current efficiency is from 90% to 95%. The current density varies from 15 to 25 amperes per square foot.

As the anodes dissolve, the impurities either drop out as an insoluble slime or pass into solution. Theoretically those elements more electronegative than copper should be in solution and those more electropositive in the slimes. Practically the situation is not simple, owing to the presence of alloys and precipitation of impurities as insoluble compounds. Slimes are made up of varying amounts of copper, silver, gold, arsenic, antimony, lead, selenium, and tellurium, with traces of nickel. Silver in the anodes is combined with selenium and tellurium, and these compounds are insoluble. Any excess of selenium and tellurium will form insoluble copper compounds, and some copper is precipitated by the discharge of cuprous ions in the solution. Gold and the uncombined silver go into the slimes, and the lead that dissolves forms a precipitate of lead sulfate. Antimony forms a basic arsenate, which accounts for the presence of arsenic in the insoluble material. The important impurities that accumulate in the electrolyte are arsenic, in the form of arsenic acid, and nickel sulfate. At some of the refineries the electrolyte containing impurities is electrolyzed in a series of tanks equipped with insoluble anodes. Copper is recovered as a deposit on the anodes; arsenic is largely in the slimes; and nickel sulfate is recovered from the solution. In other refineries the electrolyte is evaporated to 42° Bé and 90% of the copper crystallized as a crude copper sulfate; mother liquors are a source of nickel.

The slimes are roasted and the copper is removed by dissolving the copper oxide with sulfuric acid. The residue is subjected to a furnace refining for removal of lead, antimony, selenium, and tellurium. The residue, known as Doré metal, is mainly silver with varying but rela-

tively small amounts of gold. A typical Doré metal contains 98.5% silver and 1% gold, the remainder being metallic impurities.

Nickel. Nickel anodes result from a pyrometallurgical process involving the smelting of a matte containing nickel and copper, separation of nickel sulfide, roasting, and reduction of the oxide in an open-hearth furnace. The starting sheets on which the refined nickel deposits are aluminum. The cathodes are enclosed in chambers made of wood and canvas. The electrolyte that is fed to the refining tanks contains nickel sulfate and boric acid. During electrolysis the nickel content of the electrolyte must be maintained by addition of nickel sulfate. The electrolyte is freed of copper and iron, neutralized by nickel carbonate, and returned. The anode slimes, composed largely of nickel and copper, are melted and made into anodes for a second electrolysis, and the slimes from this process yield platinum and other precious metals of this group.

Lead. In the electrolytic process for refining lead, the electrolyte contains lead fluosilicate, PbSiF_6 , and hydrofluosilicic acid, H_2SiF_6 ; and deposition is on sheet lead cathodes. Tin must be removed before the anodes can be used. The common impurities, which are rarely over 2%, are mainly found in the slimes.

Silver. This metal is obtained to a very considerable extent as a by-product from the electrolytic refining of copper, and from lead refining by the Parkes process described in the chapter on Metallurgy. It also is produced along with gold directly from the ores of these metals. The refining of silver differs from that of the other metals in that the deposit is in the form of relatively large and loosely adhering crystals which are scraped from the cathodes. The anodes are enclosed in canvas to prevent contamination of the deposit of silver by the slimes. Cathodes are either of alloy steel or of graphite. The electrolyte contains silver nitrate and copper nitrate. Gold is the most valuable metal left in the insoluble residue.

Gold. Electrolysis in the refining of gold is in a solution of auric chloride containing hydrochloric acid. The main impurities in the gold anodes are platinum and palladium, which remain in solution. The cathodes are gold sheets, and the deposit is of a high degree of purity (from 99.98% to 100.00%, referred to as 999.8 to 1000.0 "fine"). The insoluble solids that accumulate are silver chloride, lead sulfate, some of the rarer metals of the platinum group, and gold formed by discharge of aurous ions in the solution. Platinum and palladium are recovered from the electrolyte. Where anodes have a high silver content (6% or higher), superimposing an alternating current on the

direct current removes the interfering and insulating layer of silver chloride.

Some progress has been made in the electrolytic refining of *bismuth*, *antimony*, and *iron*. When the price justified the method, *tin* was electrolytically refined from low-grade material made from complex and impure ores, and in some countries, but not in the United States, tin is removed from tin plate scrap by electrolytic methods.

Electroplating and Electroforming Processes. Electroplating refers to coating by electrolytic means a metal that lacks certain qualities, such as appearance and resistance to wear and corrosion, with a thin layer of a metal of superior qualities. The metal to be coated is made the cathode, and the coating metal is obtained either from anodes or from soluble compounds of the metal, insoluble anodes being employed.

The object or article to be plated must be thoroughly freed of adhering corrosion products or other substances that would interfere with the adherence of the deposit. This is accomplished in a variety of ways, including mechanical abrasion, the action of acids (pickling), soaps, alkalies, and organic solvents, and electrolytic solution methods.

The crystalline nature of the deposit depends on the crystal structure and the form of the metal to be coated, the composition and concentration of the electrolyte, and the current density. In addition to compounds of the metal to be plated, the electrolyte may contain other salts to increase conductivity, materials that prevent passivity at the anode, substances of a colloidal nature that function in small amounts to hinder formation of large crystals, and buffers to maintain the correct hydrogen ion concentration. Low concentrations of the ions of the metal to be deposited are commonly necessary in order to insure a fine crystalline structure of the deposit. This is generally the result of the use of double salts and compounds giving complex ions in which the metal is in the negative ion. In some plating operations the base metal is coated electrolytically by successive layers of different metals, and the simultaneous plating of two metals as an alloy is often carried out.

Copper may be plated on metals more electropositive than itself by the use of copper sulfate-sulfuric acid electrolytes, but on more electronegative metals the copper ion concentration must be lowered by the use of cyanides in alkaline solution, the copper ion resulting from secondary ionization. If the coating is to be of considerable thickness, after a preliminary coating from a cyanide bath the deposit may be built up from an acid-sulfate bath. *Nickel* is plated from

solutions containing sulfates, chlorides, boric acid, and ammonium salts. The pH value is around 5.3 unless part of the nickel anodes are replaced by insoluble lead anodes, when a value of 3.0 is employed. *Iron* has a limited use in electroplating, its most important function being to build up worn machinery parts. *Zinc* is electroplated extensively on electrical cable and mains as a protective coating. The greatest users of electroplated *tin* are the automobile and electric refrigerator industries. *Cadmium* is plated on steel from a cyanide bath. *Gold* and *silver* are plated from potassium cyanide solutions in which double cyanides of these metals are formed. Gold is often alloyed with copper, nickel, or silver in the process of electroplating by means of simultaneous deposition, the different shades being known as red, white, and green gold respectively.

Chromium forms a very smooth surface, which is also quite hard. It is thus very valuable where oxidation and tarnishing would destroy the mirror-like finish and alter the color of many other metallic coatings, and also where resistance to wear is essential. Chromium is applied in extremely thin layers, since thicker layers tend to develop cracks and other imperfections. These layers are somewhat porous and do not protect the underlying metal from corrosion. It is accordingly necessary to coat such metals as iron with a layer of copper, and on this plate a layer of nickel, which resists the action of the baths used in chromium plating. Chromium is then plated on the nickel. The electrolyte contains about 250 grams of chromic acid per liter and small amounts of sulfates. Lead anodes are used and current densities are quite high. The voltage is above the decomposition potential of water; a film of hydrogen is maintained on the surface being plated; and something like 70% of the current is used in hydrogen production.

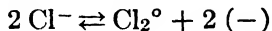
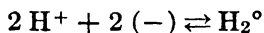
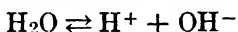
The distinction between electroplating and electroforming is that in the latter process a metal coating is placed upon a removable mold so that the entire object or plate is of the same metal throughout. Since the bulk of electrolytic deposition on molds is in connection with making metal plates for printing books, the term "electrotyping" is often used to include all such operations. Metal molds coated with graphite and other materials such as sulfides, chromates, and silver iodide to insure their ready removal find considerable use, but wax molds are the rule in the printing industry. The type and engravings are assembled in desired form and covered with graphite; on this is poured a thick layer of molten beeswax, vegetable wax, or ozokerite, usually with minor amounts of other materials to give greater plasticity. Pressure up to two tons per square inch is applied, so that the

wax takes a clear impression of every line in the engravings and the exact form of the type. The mold is then removed from the type and engravings, and its surface is coated with a very thin layer of graphite. In order to develop a surface that will uniformly conduct the electric current, the molds are placed in a solution of copper sulfate, and a very thin and fragile layer of copper is precipitated by the use of iron filings. The coated molds are then placed in the plating bath, in which are copper anodes, and a layer of metal of the desired thickness is produced by electrolysis. Somewhat the same method is used to make metal plates from which phonograph records are stamped.

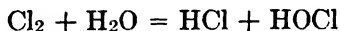
Production of Non-Metals. The non-metals liberated from their compounds on commercial scale by electrolysis of aqueous solutions are chlorine, hydrogen, and oxygen. The two last-named substances are obtained by other methods on a much larger scale than by electrolysis, but the use of electric current is now the only commercial method for the production of chlorine.

Chlorine. Chlorine is made along with metallic sodium by the electrolysis of fused sodium chloride, but since the production of sodium is small, the bulk of the chlorine is from the electrolysis of aqueous salt solutions.

The simple reactions which result in the simultaneous production of chlorine and hydrogen are:



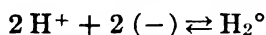
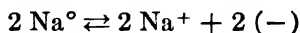
The tendency of hydrogen ions to take up electrons is so much greater than that of sodium ions that metallic sodium is never actually formed unless a cathode is used that has a high overvoltage for hydrogen and can at the same time take up sodium to form a relatively stable alloy. With practically saturated salt solutions there is very little tendency for oxygen to be formed by the discharge of hydroxyl ions, the overvoltage of chlorine being low on graphite anodes. Chlorine reacts slowly with water to form hydrochloric and hypochlorous acids.



This reaction is greatly accelerated in the presence of hydroxyl ion. The hypochlorite ion undergoes various reactions, the net result being the formation of chlorides, chlorates, and oxygen. Hence it will be

seen that one of two things must be done to prevent loss of chlorine and the formation of undesirable by-products. Either hydroxyl ion must be kept low, or the products of electrolysis must be kept apart as far as possible. The first result may be accomplished by forcing the discharge of the sodium ion rather than hydrogen ion by the use of a mercury cathode, the amalgam formed being removed from the cell while still quite low in sodium. The second expedient is most generally used in the chlorine industry. It is impossible to keep the products of electrolysis completely apart and at the same time to decompose all the sodium chloride in the cell. A compromise is reached in which somewhat less than half of the chloride ion is converted to chlorine, and only very little of the chlorine is used up in side reactions. Chlorine and hydroxyl ions are separated first by flowing the electrolyte through the cell so that it escapes after contact with the cathode, and in the second place by hindering backward diffusion and migration by means of diaphragms. When concentrated in multiple-effect evaporators, the cell effluent readily deposits its sodium chloride and gives a solution of practically pure sodium hydroxide.

The advantage of a *mercury cathode cell* is that a very pure sodium hydroxide is obtained without necessity of salt separation, but this is more than counterbalanced by the expense of handling mercury and the great investment in this metal. The amalgam is removed from the electrolyzing compartment of a mercury cathode cell, brought in contact with water, and decomposition is accelerated by the passage of an electric current from a cathode through the liquid, and through the amalgam, which functions in the decomposing compartment as an anode. The reactions in this secondary discharge cell result in the production of caustic soda and liberation of hydrogen.



In diaphragm cells a diaphragm must be sufficiently porous to permit easy passage of ions, but at the same time the orifices that are filled with liquid must be so small that diffusion is relatively slow. The most widely used diaphragm material is asbestos, either as a fabric or as a paper. The diaphragms are held very close to the cathodes, which are either perforated steel sheets or heavy copper screen.

The essential features of a diaphragm cell are: a closed tank or

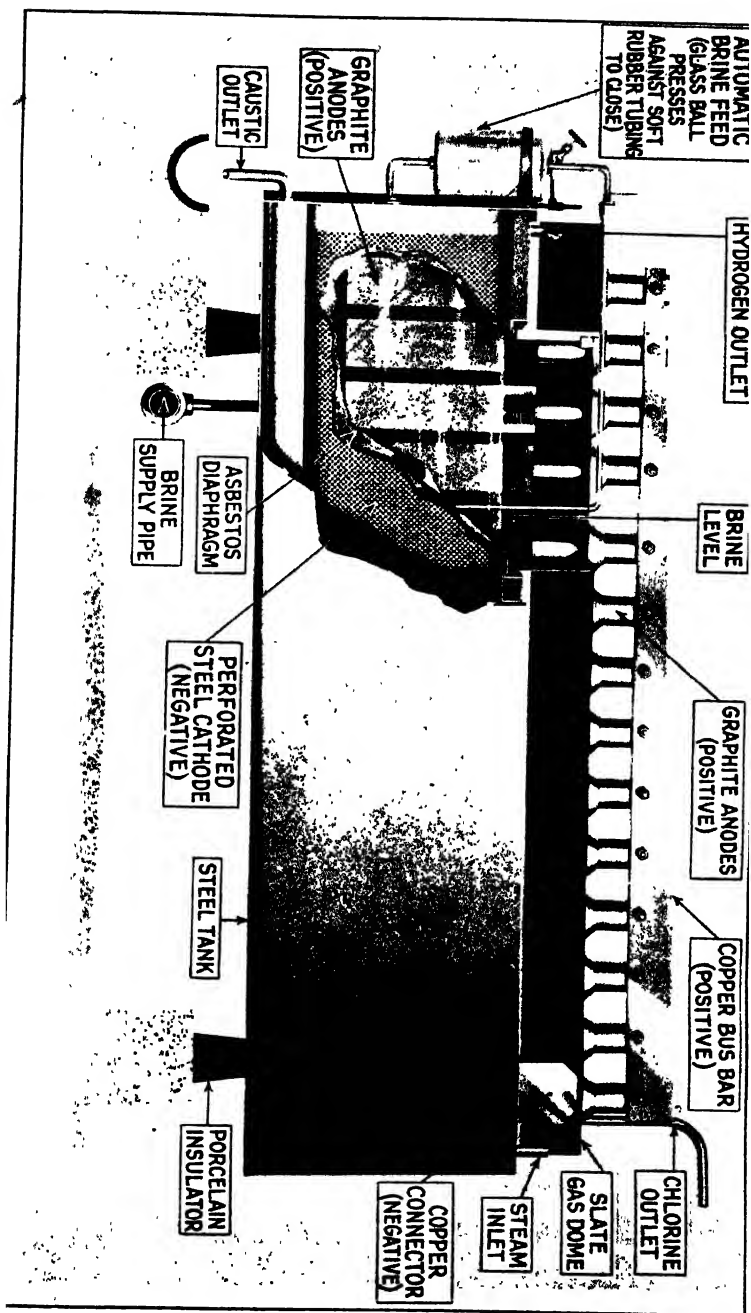


Fig. 1. Nelson Chlorine Cell. Courtesy Mr. H. R. Nelson, New York City.

container, which is either rectangular or cylindrical; a series of graphite anodes in the inner compartment, from which chlorine is discharged, the gas escaping from this compartment through suitable outlets; one

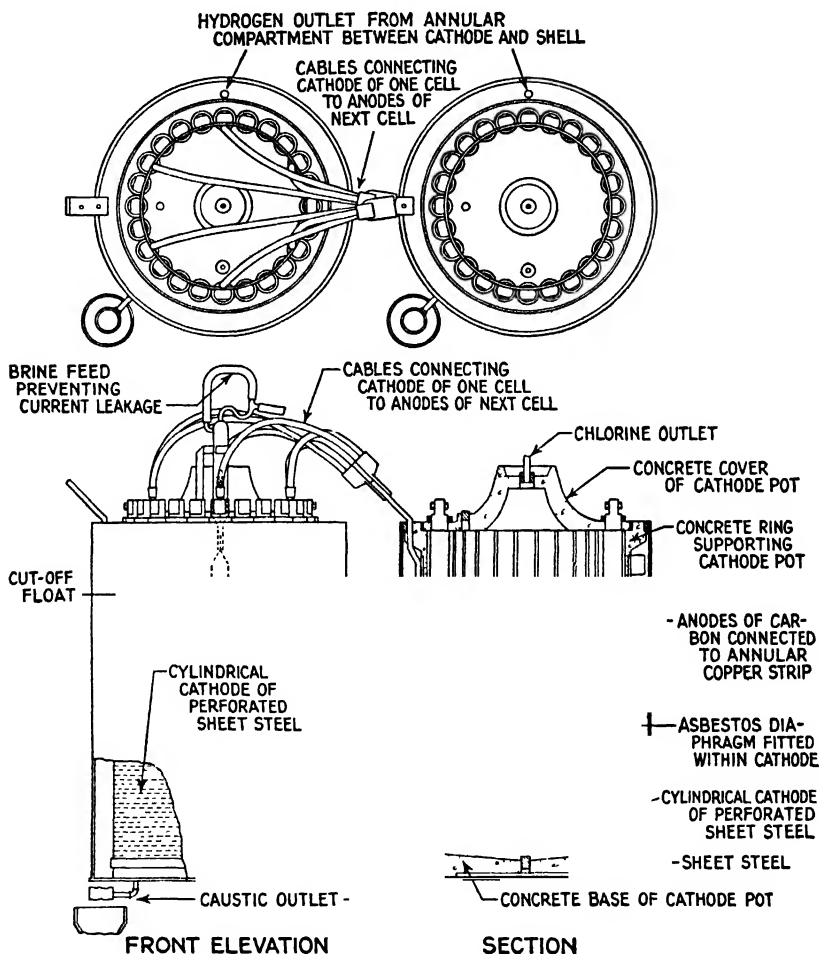


Fig. 83.—Vorce Chlorine Cell. Courtesy Westvaco Chlorine Products, Inc., South Charleston, W. Va.

or two cathodes separated from the inner anode compartment by intervening diaphragms; and an outer compartment, from which hydrogen gas escapes and from which the solution of sodium hydroxide and undecomposed sodium chloride is drawn. In most cells in commercial use in the United States the outer or cathode compartment is empty, the

cells being known as the "unsubmerged cathode" type. The electrolyte percolates slowly through the diaphragm and runs down the surface of the cathode. One cell employs carbon dioxide in the cathode compartment to convert the sodium hydroxide to sodium carbonate. Another fills the space with kerosene so that the escaping electrolyte forms drops, the difference in specific gravity of the liquids inside and outside giving some hydrostatic head to the electrolyte in the inner compartment.

Cells vary from 800 to 4000 amperes capacity, and the voltages range from 3.4 to 4.2. Current efficiencies are from 90% to 96%, the

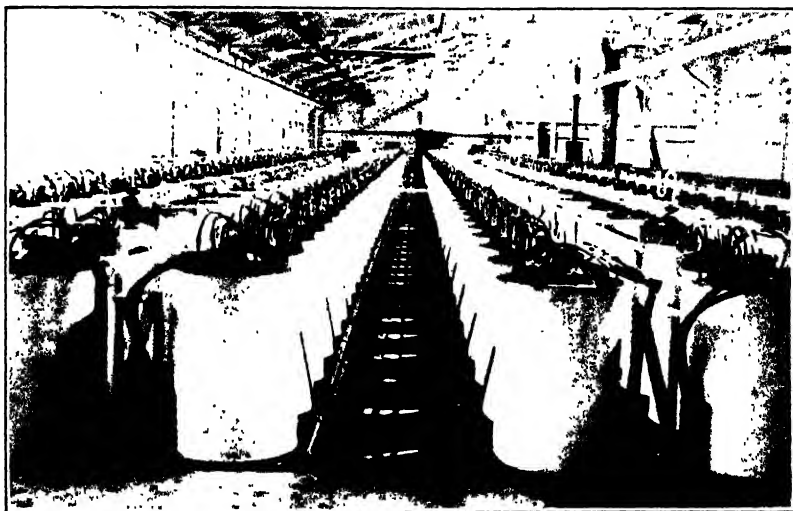


FIG. 84.—An Installation of 560 Vorce Cells. Courtesy Westvaco Chlorine Products, Inc., South Charleston, W. Va.

average approaching the higher figure. The energy efficiencies vary from 50% to 64%, some of the more modern cells averaging well over 60%. Economical salt decomposition is between 40% and 60%, but is ordinarily less than 50%. The brine fed contains about 300 grams per liter, and the effluent usually has somewhat more than 100 grams of sodium hydroxide per liter. Hypochlorites are reduced by the escaping hydrogen to chlorides. Sulfates are rigidly excluded because of the effects of oxygen discharge on the anodes. In spite of careful purification of brine, all diaphragms have to be washed or renewed at intervals.

Chlorine finds its chief use in the bleaching of fibers from which paper and textiles are produced. About 65% of all chlorine is used in

the paper industry and 22% in the textile industry; sanitation, including sewage effluents and public water supplies, accounts for another 10%. Chlorine has a great variety of uses in the chemical industry. In the World War chlorine played a most important part, since most war gases involved the use of chlorine in their manufacture, and the Dakin-Carrel solution used in irrigation of open wounds and as an antiseptic is made by the action of chlorine on sodium carbonate solutions.

The purely chemical methods of making chlorine have been almost entirely abandoned, partly because they made chlorine very much diluted with air, and also because they required hydrochloric acid. The Weldon process employed complex manganites and hydrochloric acid with air regeneration of the oxidizing agent. The Deacon process depended on the catalytic action of copper chloride on a mixture of air and hydrogen chloride.

Chlorine made by these two methods was so dilute that it could not be profitably liquefied. Since the bleaching and disinfecting action of chlorine is only realized after it is converted to hypochlorite (OCl^-), it was common practice to take up the chlorine in slaked lime to form "bleaching powder," also incorrectly called "chloride of lime." The main component of commercial bleaching powder is a double salt of hydrochloric acid and hypochlorous acid, $\text{CaCl}(\text{OCl})$. With the modern electrolytic method of chlorine production, much less is made into bleaching powder than formerly, the use of this material being largely confined to many small plants whose requirements are intermittent, and for local disinfection. Most chlorine is now compressed and liquefied with the aid of refrigeration, and is handled in steel cylinders ranging in capacity up to 15 tons, and in tank cars. Liquid chlorine has a vapor pressure of about 100 lb. at 20°C ., and there is so much cooling during its evaporation that its discharge is readily controllable. Bleaching solutions are made by treating sodium hydroxide or sodium carbonate solutions, or more commonly calcium hydroxide suspensions, with chlorine. The heat of reaction is utilized by passing the chlorine through coils immersed in the tank in which the reaction is taking place, and in this way the cooling effect of evaporation is reduced. Ordinary bleaching powder has up to 35% "available chlorine," but recently a product has been made that contains considerable calcium hypochlorite and runs as high as 65% available chlorine.

Available chlorine refers to the chlorine present in a compound as hypochlorite. It is calculated in terms of the chlorine as hypochlorite produced by pure chlorine, which is one-half of its weight. Calcium

hypochlorite, $\text{Ca}(\text{OCl})_2$, has a molecular weight of 143, and out of 143 lb. of the pure salt, 71 lb. represent chlorine as hypochlorite. When 143 lb. of pure chlorine react with water in the presence of something that will take up the oxygen formed by the decomposition of hypochlorite ion, the hypochlorite chlorine represents 71.5 lb. Thus pure calcium hypochlorite is equal practically pound for pound to pure chlorine, and would be said to have over 99% available chlorine.

Bromine is obtained by the action of chlorine on brines high in bromides from which chlorides have been partially removed by evaporation and crystallization. Iodine is made by the action of chlorine on soluble iodides obtained from natural brines, and also from the iodates found in crude Chilean sodium nitrate, acid sulfites being employed for its liberation.

Sodium and potassium chlorates are very generally made by electrolysis of brine. The hypochlorite ion formed by the action of chlorine on hydroxyl discharges to form chlorate. Every facility is offered for the mixing of the primary products of electrolysis, cathodes and anodes being placed very close to each other. Cathodes are of iron, but the anodes are of platinum, and where temperatures are kept low they may be of graphite. Hydrochloric acid is continually added to maintain slight acidity, and dichromates are also present. Sodium chlorate is the main product of this process, the cell liquor reaching a concentration of 750 grams per liter of this salt before it is removed. Potassium chlorate is much less soluble, hence the electrolyte is circulated and the crystalline material removed outside the cell before return of the liquid. Perchlorates and hypochlorites are also made by electrolytic methods, but electrolytic hypochlorite is not used to any extent in the United States.

Hydrogen, Oxygen. Hydrogen and oxygen are made at the same time by electrolysis of sodium hydroxide solutions. It is of course very necessary that the two gases do not mix. This is readily avoided in the operation of the cell by the use of asbestos diaphragms. There are several types of cells, one being a single unit in which there is one anode and two cathodes, another a multiple cell made up of a series of bipolar plates separated by diaphragms and held together much after the fashion of a plate and frame filter press, and a third made up of a series of electrodes separated by diaphragms and equipped with gas-collecting bells. Some pressure cells are in use. Accidental reversal of polarity is rendered practically impossible by safety devices at the switchboard. Since the cost of oxygen from liquid air is low, oxygen may be regarded as a by-product. Hydrogen can ordinarily be

prepared on a large scale more cheaply from water gas, but the process is not adapted to small-scale operations.

Electrolytic chlorine cells produce hydrogen, and there is an increasing tendency to use this gas commercially. Some larger concerns are developing industries for the purpose of utilizing by-product hydrogen. The most promising outlet for hydrogen of this sort is in ammonia and methanol syntheses.

Ammonia may be readily compressed and liquefied, and ammonia gas may be easily decomposed quantitatively into nitrogen and hydrogen. The diluting nitrogen, which is only one-fourth of the volume of the gases, does not interfere in many processes in which hydrogen is used. Hydrogen cannot be liquefied at ordinary temperature, and so only limited amounts of it may be handled as a gas under heavy pressure. Liquid ammonia is thus a very convenient source of cheap and easily transported hydrogen.

Organic Compounds. The electric current finds a limited use in the synthesis of organic compounds, but such methods are restricted to relatively rare and high-priced organic chemicals. Its greatest use is in reduction reactions. Electrolytic oxidation is largely limited to regeneration of inorganic oxidizing agents. Halogenation by continuous production of chlorine electrolytically in the presence of organic compounds is employed profitably in a few instances, such as the production of iodoform and bromoform.

Electrolysis of Fused Compounds. When fused substances are electrolyzed, the resistance of the bath may be employed to maintain or assist in maintaining the required temperature, thus using the current to bring about chemical reactions and to generate heat. Sodium, potassium, calcium, magnesium, and aluminum are produced by this method.

Sodium. Fused sodium chloride and fused sodium hydroxide are the sources of metallic sodium. When the hydroxide is used, there must be very close temperature regulation, and electrolysis must be carried out at a temperature not more than 10° above the melting point of the hydroxide. Because of high surface tension, molten sodium may be retained by gauze diaphragms and removed from the cell by a gauze ladle. The cell is equipped with an iron cathode in the form of a thick rod, which projects up into the electrolyte to a short distance from its surface. Around it is a diaphragm of iron gauze, which extends well above the molten caustic and terminates in an iron cylinder. The anode is in the form of a ring. Gas flames supplement the heat developed by the resistance of the bath.

In recent years, sodium hydroxide cells have been largely replaced by sodium chloride cells for the simultaneous production of sodium and chlorine. The melting point of sodium chloride (804°C.) is lowered by addition of other salts to less than 600°C. The electrolysis is carried out at operating temperature of 600°C. , this being maintained and electrolysis carried out by direct current. In a commonly used fused chloride cell the cathodes are of iron and are separated from the graphite anode by gauze diaphragms. The molten metal overflows from the cathode compartments, and the chlorine is removed from an iron bell above the anode. The annual production of metallic sodium in the United States is of the order of 5000 tons. Sodium is used in making peroxides, cyanides, and sodamide, and has extensive use in organic syntheses. Potassium may be obtained by the same methods.

Calcium. This metal is produced in very small amounts, since it has few industrial uses. The method employed is to electrolyze fused calcium chloride. A water-cooled iron cathode at the outset of a run just dips below the surface of the molten electrolyte, but is gradually raised as the calcium adheres and solidifies, the metal itself serving as the cathode. This is called the "contact electrode" principle. Owing to the presence of a basic chloride and the solubility of calcium it is necessary to change the electrolyte at frequent intervals. Calcium and barium are alloyed with lead to make useful bearing metals, and these alloys may be made by electrolyzing the fused halides with lead cathodes.

Magnesium. Magnesium oxide may be dissolved in molten fluorides and the solution electrolyzed, the metal being withdrawn at intervals, but this method has been generally supplanted by the fused chloride process. In the United States, magnesium to the extent of 1,300,000 lb. per year is made by the electrolysis of carefully dehydrated and fused magnesium chloride containing sodium chloride. The cells are large cast-steel pots functioning as cathodes, and anodes are of graphite. The metal floats to the surface and is protected by a film of molten salt. A heavy sludge containing magnesium oxide sinks to the bottom. The process is essentially continuous, the electrolyte being added at intervals and the metal being removed daily. The heating effect of the current is supplemented by external heat. The product is from 99.95% to 99.99% pure magnesium. Crude magnesium may be purified by sublimation under reduced pressure.

Aluminum. This valuable and abundant metal is obtained by dissolving carefully purified alumina, Al_2O_3 , in fused cryolite, $3\text{NaF} \cdot \text{AlF}_3$, and calcium fluoride, CaF_2 , and passing an electric current

between carbon anodes and the carbon lining of the cell, which functions as the cathode. This process was simultaneously developed by Heroult in France and Hall in the United States. It is interesting to note that the difficulties experienced on a small scale largely disappeared with the use of large-size equipment.

The raw material is a hydrated alumina known as bauxite, which contains mainly such impurities as ferric oxide, titanium oxide, and silica. The widely used Bayer process for refining alumina involves digesting dried and finely ground bauxite under heavy pressure with strong caustic soda, the temperatures being of the order of 160° C. to 170° C. The alumina dissolves and the residue contains the bulk of the impurities, which may be removed by settling, decanting, and filtering. When the filtered solution is diluted and allowed to stand with the addition of a little aluminum hydroxide, hydrolysis takes place to a large extent, and a precipitate of practically pure aluminum hydroxide is formed. This product is removed by filtration, washed, and calcined; the filtrate is reinforced by caustic soda and used again. The alumina made by this process is quite pure and contains less than 0.01% ferric oxide and silica. A third method, known as the Hoopes-Hall method, is to fuse bauxite in an electric furnace with just enough carbon to reduce all the impurities and a little of the alumina. An alloy is formed on which floats a relatively pure alumina. By blowing air and steam through the molten alumina some ferric oxide is volatilized, iron carbide is oxidized, and the alumina is obtained in the form of thin-walled globules. These are leached with sulfuric acid to remove lime and titanium, leaving a product from which 99.4% aluminum can be made.

The electrolysis is carried out in iron cells heavily lined with carbon. The anodes, made from hard-pressed and baked carbon from petroleum coke, are suspended in the electrolyte and reach within a few inches of the molten metal at the bottom of the cell, which itself serves as the cathode, the current passing from the metal through the lining, being distributed by soft steel plates imbedded in the lining. The anodes are gradually destroyed by the liberated oxygen, from 0.8 to 1.0 lb. of carbon being used up per pound of aluminum made. The electrolyte is a mixture of sodium, aluminum, and calcium fluorides. Hydrofluoric acid with a mixture of bauxite and soda results in a synthetic cryolite, which may be used instead of the naturally occurring mineral. The density of the solution of alumina in cryolite at the temperature of electrolysis (950° C.) is about 2.1; molten aluminum has a density of 2.3. The amount of alumina dissolved in the bath is

from 2% to 5%. The alumina is denser than either cryolite or aluminum, but is finely divided and is held in suspension by the stirring effect of escaping gases and by the effect of the magnetic field. A

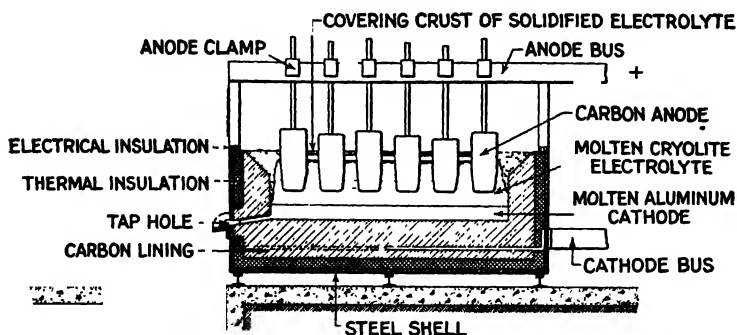


FIG. 85.—Aluminum Cell. Courtesy Aluminum Company of America, New Kensington, Pa.

crust of frozen electrolyte covers the molten bath, and on this rests a supply of calcined alumina to be preheated. When alumina is low, the electrolyte no longer “wets” the anodes, a gas envelope is formed

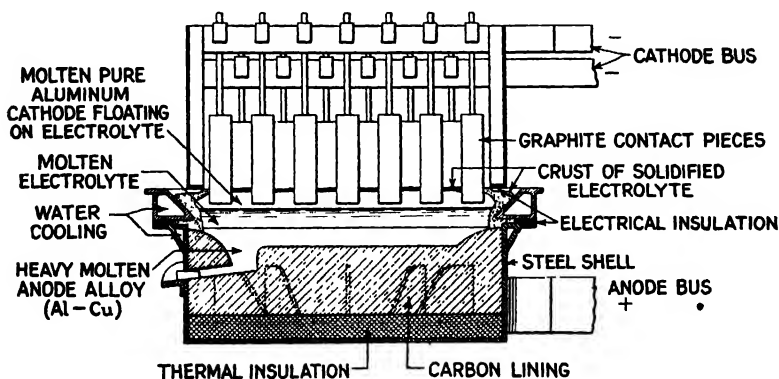


FIG. 86.—Aluminum Refining Cell. Courtesy Aluminum Company of America, New Kensington, Pa.

around them with arcing, and the resistance is greatly increased with consequent rapid rise in voltage. This is the “anode effect” common with fused electrolytes. A lamp on a shunt circuit across the cell burns

more brightly when the resistance of the cell increases, and is a signal that more alumina should be stirred into the bath. Molten aluminum is withdrawn at intervals from the bottom of the cell. A single cell uses from 10,000 to 30,000 amperes at 5 to 7 volts. Cells are connected in series of 30 to 100, so that the generator voltage is from 200 to 600. It is estimated that for each kilowatt-hour required for electrolysis about 2.5 kw-hr. are used in heating.

Impure aluminum may be refined by alloying it with copper and silicon and allowing this molten alloy to function as an anode. The electrolyte in this case is cryolite saturated with alumina whose density is increased by barium fluoride so that the refined metal will float upon it as it is formed at the cathodes. The pure molten aluminum is protected by a crust of solid electrolyte containing alumina. As the aluminum is used up from the molten anode, more impure metal is supplied to take its place, and pure metal is withdrawn.

Electric Furnace Operations. A great many chemical operations are carried out at high temperatures produced by the electric current. Some of these are described in other chapters. Practically all the iron alloys that are used to introduce metals into various steels are made in the electric furnace by reduction of the oxides of these metals by carbon or silicon in the presence of iron. In each of these the element associated with iron predominates in amount, the iron serving largely to lower the melting point and make it easier to introduce the desired metal into the molten steel. Among these electric-furnace products may be mentioned ferrosilicon, ferrotungsten, ferrochromium, ferromanganese, ferrovanadium, ferromolybdenum, and silicomanganese.

Electric furnaces are of three general types: the *arc*, in which there is a flame of highly heated gas between two electrodes; the *resistance*, in which a poor conductor such as carbon becomes intensely hot by the passage of an electric current, transferring most of its heat by radiation; and the *induction*, in which a primary coil produces current and high temperature in a solid resistor or molten metal, which acts as a secondary coil. An induction furnace has been described as a "step-down transformer with a short-circuited secondary coil." All furnaces commonly use alternating current, but the induction furnace is limited to alternating current alone. There are also combination arc-resistance furnaces. Electric heat is economical for temperatures below 1400° C. only where power is very cheap and fuel scarce. It is particularly adapted to the production of very pure substances in small amounts with very close control.

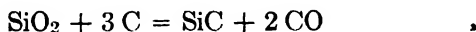
The more important industries using the electric current to produce

heat or gaseous ionization are briefly described in the following paragraphs.

Nitrogen Fixation. The arc process, which uses the largest quantity of electric current per unit weight of product, now plays a minor part in the field of nitrogen fixation. The calcium cyanamid process uses an electric furnace to make calcium carbide, and the operation in which calcium carbide reacts with nitrogen requires some current. Sodium cyanide results from fusing sodium chloride and calcium cyanamid in an electric furnace. Since most of the fixed nitrogen of the world now comes from direct ammonia synthesis, the fixation of nitrogen can hardly be called an electrochemical industry.

Fused Alumina. When aluminum ore is heated in a combination arc and resistance furnace with partial reduction and removal of the reduced impurities as a metallic slag, the main product is a crystalline and highly resistant form of alumina. If the raw materials are practically pure hydrated alumina, no slag is produced. The furnace consists of a hearth of carbon blocks, a movable shell fitted into a groove in the hearth, and a set of electrodes. The arc is first formed between the hearth and the electrodes, but as the charge is introduced the arc is ultimately between the electrodes. The electrodes are gradually raised as the reactions take place. At the end of the operation the electrodes are removed, the product cooled in the form of a block and the shell of the furnace is lifted from around it. Fused alumina is used in making such laboratory equipment as crucibles, filter cones, pyrometer tubes, combustion boats and tubes, muffles, and furnace cores, as a refractory in larger-scale equipment, and as an abrasive.

Silicon Carbide. Crystalline silicon carbide was discovered by E. G. Acheson, who first made it by heating clay impregnated with carbon to a high temperature. The product is commonly known by the trade name "Carborundum." The present method uses coal or coke and silica. The reaction usually given to account for its formation is



A typical 2000-h.p. furnace is 47 ft. long, 8 ft. wide, and 8 ft. deep. The voltage is from 200 to 300. Theoretically, 4700 kw-hr. are required per metric ton of silicon carbide, but the current actually required is about 8400 kw-hr. The furnace is built up for each run and torn down to remove the products. It is essentially a brick hearth as a foundation, on which are built four brick walls to form a long box. The side walls are curved so that the cross section of the charge is

roughly circular. In the end walls, which are made up largely of Carborundum brick, are carbon plates, to which copper bus-bars are connected. No fireclay is used between the firebricks, which are held in place by a steel frame. A charge of sand, sawdust, coke, and salt is shoveled in until the furnace is nearly half full. The sawdust in its decomposition gives off gases, which give porosity to the charge; salt causes the formation of volatile chlorides of the elements regarded as impurities. Some manufacturers prefer to use purer materials and omit salt. Instead of sand, unconverted material from a previous run may be partially or wholly substituted. A resistor of granular carbon of approximately cylindrical form is laid between the end connections, and the rest of the charge is put in until the furnace is heaping full.

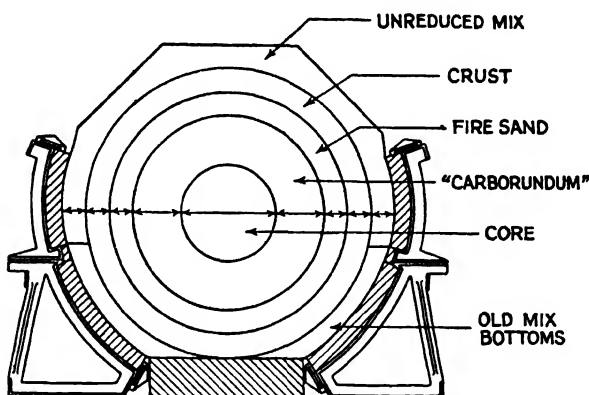


FIG. 87.—Cross Section of Silicon Carbide Furnace. Courtesy The Carborundum Company, Niagara Falls, N. Y.

Within one day the temperature will have risen to the desired maximum. It is regulated so that this temperature is maintained for the length of time necessary to bring about all the chemical changes that can be profitably secured. The carbon monoxide burns as it escapes from the charge. The current is cut off and the furnace cools for a period of four days. The charge is dug out, the first material being unchanged reaction mixture. Next is found a variety of silicon-carbon-oxygen compounds that have some value. Below this is uncrystallized silicon carbide, which may also be used for furnace linings and crucibles. The main product is crystalline silicon carbide. The crystals are a bluish black, owing to a film of silica, pure silicon carbide being colorless, and are very hard. Thus this material finds extensive use as an abrasive. Its heat conductivity is comparatively high, and in

furnaces it must be backed up by insulating brick. It is highly resistant to chemical change even at high temperatures, and is extensively used as a furnace or firebox lining, being cooled by air flues or water pipes. The core, or resistor, is completely converted to graphite during the operation. Other silicon carbide products include those made by imbedding carbon articles in silica and heating in a resistance furnace with the formation of a surface coating of carbide, and fine threads of silicon-carbon-oxygen compounds produced by diffusion of carbon monoxide into silicon vapor.

Graphite. The so-called amorphous form of carbon typified by lampblack, gas carbon, and petroleum coke is proved by the X-ray to be identical in its atomic space lattice with graphite. It can be converted to graphite at the temperature of the electric furnace, but the transformation is slow unless metallic catalysts are used. Such metals as iron act probably by intermediate formation of carbides and their decomposition into graphite and free metal. Impurities volatilize from the carbon during the process, and the ash left in electrical furnace graphite is negligible. The commercial method of making artificial graphite is to heat substances that are largely carbon, containing a little iron, to a temperature of 2200° C. or higher. This is accomplished by making the raw material the resistor of an electric furnace. The carbon is in the form of a loose powder, or is molded into rods or plates and the space between them is packed with loose carbon. The ends of the furnace, at which connections are made, are water cooled. The initial current is ordinarily around 200 volts, and amounts to 4000 amperes. At the end of 24 hours the amperage has increased to 9000 but the potential has decreased to 80 volts. A furnace rated at 1000 h.p. has an inside length of 30 ft. and a diameter of charge of 2 ft. By varying conditions it is possible to produce a dense, hard graphite to be used in electrodes, or a very soft and finely divided material suitable for lubricants.

Calcium Carbide. At temperatures between 1800° C. and 2000° C. the following reaction, $\text{CaO} + 3\text{C} + 108,000 \text{ calories} = \text{CaC}_2 + \text{CO}$, goes predominately to the right. At higher temperatures it reverses with the intermediate formation of metallic calcium and free carbon, and the reduction of carbon monoxide by calcium to give calcium oxide and more carbon. Hence both of the starting substances are found as a dust in the gas that escapes from a calcium carbide furnace.

The raw materials used in making calcium carbide are mainly oven coke and quicklime. Phosphorus in the coke is the most objectionable impurity, since calcium phosphide formed in the furnace produces

phosphine, PH_3 . Iron from the coke and silica from the limestone form ferrosilicon, which separates from the molten carbide and may be hand picked from the cold carbide. Magnesia, silica, and alumina should be quite low in a satisfactory limestone, so that the calcium carbide content should not be less than 97%.

Modern carbide furnaces are continuous in their operation, the finely ground mixture of lime and coke being fed into them and molten carbide being tapped from them either at frequent intervals or continuously. The furnaces are steel boxes lined with refractories next to

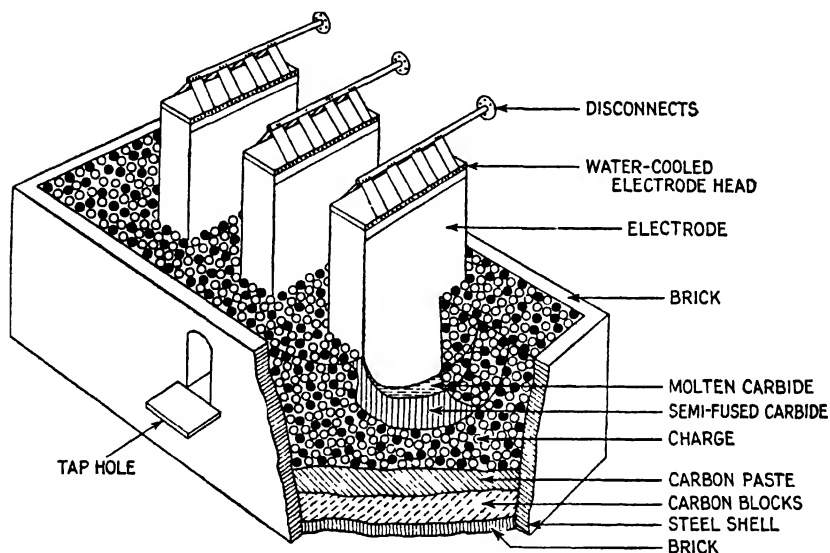


Fig. 88.—Diagrammatic Sketch of Three-Phase Calcium Carbide Furnace.
Courtesy American Cyanamid Company, New York City.

the steel and carbon next to the refractories. The charge also serves to protect the lining, since carbide is produced only in a short radius of 1 to 3 ft. around each electrode. The current used may be either one or three phase. The furnaces are of the arc-resistance type, often referred to as "smothered arc-resistance." The electrodes are of carbon and gradually react with the quicklime and are used up, the rate of decomposition being of the order of 40 to 60 lb. per ton of crude carbide. With one type of electrode arrangement a single electrode made up of a number of carbon plates is suspended in the furnace while a set of electrodes lie horizontally on the bottom of the furnace and constitute a conducting hearth. In the type commonly used in this country the hearth is neutral or non-conducting and a series of

electrodes are suspended in the furnace. The tops of the furnaces may be open, but when closed the furnace gases and dust are collected and used.

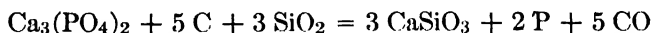
Voltages vary from 100 to 150 according to the size and type of furnace. One very important producer of calcium carbide now uses 50,000-h.p. furnaces with a capacity each of 185 tons of carbide per day. A single-electrode furnace using as high as 240,000 amperes has an electrode 10 ft. in diameter. In another employing several electrodes, each electrode is made up of five sections 20 by 22 by 100 in., and with its holder weighs 16 tons. The most recent furnace to be installed in the United States uses 300,000 amperes. The main use of calcium carbide is in the generation of acetylene for cutting, welding, and chemical syntheses.

Carbon Bisulfide. Carbon bisulfide is commonly made by passing sulfur vapors over carbon contained in a gas-heated, vertical retort. An electric furnace process has also been used for this purpose. Coke packed between horizontal carbon electrodes at the bottom of the furnace serves as the resistor. Above the electrodes is a shaft packed with charcoal around which is an annular space through which a part of the charge of powdered sulfur is fed, so that the heat of reaction serves to preheat and melt it. The remainder of the sulfur is introduced lower down in the furnace around the electrodes. The heat developed by the resistance of the coke at the base of the furnace distills the sulfur up through the charcoal. The substances react thus:



Carbon bisulfide vapors are taken off at the top of the furnace and are condensed in the absence of air. Carbon disulfide is a valuable solvent, and is also chlorinated to produce carbon tetrachloride, sulfur chloride being a by-product.

Phosphorus and Phosphoric Acid. A mixture of phosphate rock, silica, and coke heated together in an electric arc furnace react to form a fusible calcium silicate slag, phosphorus vapor, and carbon monoxide. The following reaction represents satisfactorily what takes place:



The arc is at the bottom of the furnace between horizontal electrodes. The raw materials are fed continuously, the slag is drawn off at intervals, and the phosphorus is condensed and cast into molds. The phosphorus so made is the allotropic form "white phosphorus." Phosphoric acid is made by the same electric furnace process by adding air

to the exit gases and burning them as they issue from the furnace. Steam is added to the exit gases, and the phosphoric acid so produced is collected by electrostatic precipitation.

Ozone. A silent, high-voltage electrical discharge between plates or cylinders that are water cooled, and in most cases separated by such dielectrics as glass or mica, converts a limited amount of the oxygen of the air to ozone. The formation of an arc and the passage of sparks are prevented by filtering the air in order to avoid production of nitric acid. Ozone is used in sterilizing water, but its insolubility very greatly limits its use for this purpose. It finds its chief application as a disinfecting agent, rendering the air sterile; in rapid drying of oil varnishes; and in the bleaching of oils, fats, and textiles. Where the concentrations are so low that the air containing the ozone is breathable without discomfort, few bacteria are killed, but odors are destroyed, minute amounts of organic material being converted by oxidation into odorless substances. Ozonizers are being installed in kitchens, in public buildings, in factories such as tanneries, glue works, casein plants, and in garbage-disposal plants. The concentration of ozone varies from 0.01 to 0.1 part per million for ventilation and odor-removal purposes to 10 parts per million for rapid disinfection.

CHAPTER XVIII

METALLURGY

Metallurgy is a highly specialized field of industrial chemistry and is especially closely related to inorganic chemistry through the electro-potential series. A knowledge of the relationships involved in this series is essential in the winning of metals from their ores, and in both electrolytic and chemical methods of refining metals. The aim of all discussion of metallurgy in this book is to give very briefly the main chemical and physical principles included in metallurgical operations, and to describe the methods of producing and refining metals.

The products of the metallurgical industry are very extensively used in making the large-scale apparatus for all other chemical industries. The materials of construction of chemical engineering equipment are discussed in a separate chapter largely on the basis of those physical and chemical properties that make them suitable for use in chemical processes. The use of such products in making chemical equipment is small in comparison with the vast number and variety of uses of metals. The value of metals alone is estimated as being 10% of all manufactured products in this country. The universal use of metals in construction of buildings, railroads, ships, automobiles, machinery, and in innumerable other ways makes the products of the metallurgical industry of enormous importance.

Divisions of Metallurgy. Metallurgy falls into three general divisions: *chemical*, or the production of pure metals from their naturally occurring compounds; *physical*, including the tests of metals, the internal structure of metals and alloys, and the changes produced by heat; and *mechanical*, or the processes of shaping metals into desired forms. The third of these fields will not be considered at all, and the second only very briefly. The chemical division of metallurgy is the oldest branch of chemistry. The earliest written records of the human race reveal considerable knowledge of the production of metals, and there has also been for many centuries some understanding of the making of alloys such as bronze and steel. The progress of human civilization is intimately associated with the search for supplies of metals, the control of such supplies, and the international trading in metals. Mod-

ern science has added much to an understanding of reactions, and particularly to the economy of heat in metallurgical operations; but relatively few new chemical methods have been introduced in recent years, the most noteworthy single advance being the use of the electric current in producing and refining metals. The greatest contribution of modern science has been in the field of physical metallurgy, particularly in equilibrium studies of alloys. The pyrometer, the metallurgical microscope, the spectroscope, and the X-ray have been the instruments by which most valuable and necessary data have been obtained.

Occurrence of Metals. Most metals are found in nature in chemical combination. The common chemical compounds of metals are oxides, sulfides, silicates, and carbonates. Some of these compounds may be found in relatively pure form; many, however, are mixed with worthless minerals. That portion of ore which has no value is called "gangue." If the whole deposit contains sufficient amounts of metal to make it profitable to mine the material and put it through a production process, it is called an "ore." Modern physical methods such as flotation have rendered available certain low-grade deposits which otherwise could not have been regarded as true ores. Even those few metals which occur free are often associated with very large amounts of gangue.

Ore Dressing and Concentration Methods. The first steps in handling an ore are purely mechanical and fall into the general classification of "ore dressing." They involve various mining, quarrying, and handling methods; breaking, crushing, grinding, or disintegration operations; and, unless the ore is of exceptional richness, a concentration of the more valuable components together with rejection of those which are worthless. Gravity separation and flotation are the common concentration methods.

Production of Crude Metal from Ore. The metal may be extracted from the rich ores or concentrates by "hydrometallurgical methods," which use a cheap reagent in solution to react with the metal compounds and form soluble substances; by an electric current as means of accelerating solution of the metal compound and deposition of the metal on resistant electrodes; or by the use of high temperatures produced either by burning fuel or in an electric furnace in the presence of reducing agents such as carbon and carbon monoxide. "Pyrometallurgy," the last-named process, is by far the most widely used method.

Roasting. Carbonates and sulfides are converted as far as possible to oxides. The carbonate is decomposed by ordinary calcination either

during reduction or by separate treatment. Sulfides in general are subjected to a roasting process involving the oxidation of the sulfur to sulfur dioxide and the substitution of oxygen for sulfur in the metal compound. Roasting is carried out in separate equipment and is distinct from "smelting." Ore is heated with ample access of air. Fuel may be mixed with the charge, as in shaft furnaces; the waste products of combustion may pass over the charge, as in the reverberatory furnace; the ore may be heated in muffles and crucibles; and with certain types of ore the heat of reaction is sufficient to maintain the temperature at the necessary point, roasting being carried out in equipment resembling pyrite burners and known as "multiple-hearth" furnaces. Roasting may bring about other chemical changes, such as the decomposition of selenides and arsenides, the formation of soluble sulfates from insoluble sulfides, and the production of chlorides by the action of added sodium chloride. A purely physical change known as "sintering" is brought about by heating finely divided ore only to such a point that fusion just begins, with the result that the particles stick to each other and form lumps.

Smelting. Reduction of ore in the presence of a "flux," or material which combines with the difficultly fusible gangue of the ore to form a low-melting slag, is known as smelting. The molten metal and the slag are not miscible, and generally clear separation is possible. Coke is the most commonly used reducing agent, serving also as a fuel. Reduction is accomplished to some extent by the carbon, but for the most part by the carbon monoxide formed by the reduction of carbon dioxide by excess carbon. If the gangue is primarily silica or silicates, limestone is used to make a fusible slag. If it is composed largely of carbonates, the silica must be supplied. The smelting operation produces free elements or solutions of these elements in each other. In the case of non-ferrous metals the product may contain considerable quantities of sulfides. A mixture of metals is usually referred to as "metal," whereas a mixture of sulfides constitutes what is known as "matte." In either case the product must be refined for most industrial uses. The remainder of the ore is found in the slag, which is essentially a glass. The gases that pass off from smelting furnaces are made up of the nitrogen of the air, carbon dioxide, and some carbon monoxide. The sulfur of the ore is largely in the flue gas as sulfur dioxide. Unless the smelter is in a very isolated region, dust must be removed from waste gases. Heat is recovered from the gases of the iron blast furnace by burning them in gas engines, in waste heat boilers, and in "stoves" to preheat the air used in smelting.

There are two main types of smelting furnaces, the blast furnace and reverberatory furnace. The electric current as a source of heat in smelting is very expensive in comparison with fuels, and is used only where fuels cannot be readily obtained and hydroelectric installations are possible. When temperatures much higher than that furnished by combustion of fuel are necessary, the use of the electric current must be resorted to. The furnaces used in smelting are both of the arc and resistor types.

Hydrometallurgy. The process of "hydrometallurgy," often referred to as "wet methods," has long been the prevailing way of obtaining gold and silver, and is now increasing in application to the recovery of copper. The ore must ordinarily be finely ground, and is often roasted. It is then leached thoroughly with water or solutions of the proper reagents, and washed. The resulting solution has to be clarified by the use of filters, settling tanks, or thickeners, after which the metal is precipitated either by electrolysis or by the addition of chemical reagents, and is converted by melting into a form suitable for sale or refining. In some cases the reagent used for solution may be recovered and used again with only slight continuous losses.

Volatilization Methods. Those metals which are volatile may be recovered from their ores by reduction and distillation as in the metallurgy of zinc, and decomposition and distillation in the case of mercury. Metals may be obtained as volatile compounds, usually chlorides, which are thus removed as vapors and condensed.

Refining of Metals. Refining in general involves chemical changes on the part of those substances regarded as impurities. The most common method of refining is by oxidation, employing either oxygen from the air or combined oxygen in the form of reducible oxides of the metal being refined. Of minor importance are those reagents which combine with impurities to form a low-melting slag. Electrolytic refining is accomplished by depositing pure metal on the cathode from a solution whose concentration is maintained by the continuous dissolving of an anode of the impure metal. It is often the case that some of the impurities are so valuable that they pay the cost of refining.

Physical methods of refining involve selective fusion based on differences of melting point; extraction by means of alloy formation; distillation and sublimation. As an example of the second method, zinc is used to remove silver from lead, since the alloy formed between zinc and silver separates as a solid on the surface of the molten lead.

It is obviously impossible in one brief chapter to cover all metals

or even those of industrial importance. The five metals discussed were chosen because of their large production tonnages, and because they are typical of metallurgical methods.

The world production of "new" metal from ores is of the order of 100,000,000 metric tons yearly. Of this about 94% is iron. The four metals constituting most of the remainder are: copper, 1,800,000; lead, 1,700,000; zinc, 1,600,000; and aluminum, 250,000. It must be remembered that a very large amount of metal is remelted from scrap.

IRON

No metal has a past or present importance comparable with iron. It composes nearly 5% of the earth's crust, and a vast amount of it is found in the form of easily reducible oxides. In the United States fully 5 billion tons of iron ore are in sight and around 75 billion more are estimated as unexplored reserves, this being more than half of the world's supply. Although a great deal of this metal is recovered from scrap, some 38 million tons of iron are produced in a year in the United States. Iron suffers the great handicap of being easily oxidized in the presence of moisture. It has the advantage of abundance and ease of ore reduction. Pure iron has a number of industrial applications, but the metal is chiefly used in the form of an alloy of some sort. All sorts of properties are bestowed upon iron by relatively small amounts of other elements. Until recent years the one element most widely used with iron was carbon, but modern metallurgy includes numerous other elements such as nickel, chromium, molybdenum, tungsten, vanadium, manganese, and silicon.

Iron is found chiefly in the form of oxides, both anhydrous and hydrated ferric oxide, Fe_2O_3 , and the magnetic oxide, Fe_3O_4 . Of lesser importance are ferrous carbonate, FeCO_3 , and the sulfide, FeS_2 , or pyrite. It is very rare that an ore of less than 35% content can be profitably worked, and much higher percentages characterize the better grades of iron ore. The first step in chemical treatment of the ore is reduction in the blast furnace with the removal of most of the undesirable components of the ore as a fusible slag, and the formation of a crude iron containing 5% to 6% of other elements, most of these impurities being represented by carbon, together with about 1% silicon, 0.5% manganese, 0.1% phosphorus, less than 0.1% sulfur, and minor amounts of other elements.

The chemical changes and the reactions in a blast furnace are not simple, but may be represented here by the most important. The ore

usually contains various silicates, which for purposes of simplification may be regarded as silica. Limestone is used in the charge as a source of calcium oxide, CaO , which forms with the silica a low-melting slag. Crude carbon in the form of coke serves as fuel, as a reducing agent, and as a source of carbon monoxide, which does the larger part of the reduction. Heated air is blown in near the base of the furnace to furnish oxygen for combustion and carbon monoxide formation.

A blast furnace for iron ore is essentially a tall steel shell lined with refractory material. Its maximum diameter is about one-third of the way up from its base. The gradual increase in size from the top down to this point takes care of the expansion of the solid charge by heat, while the contraction allows for shrinkage in volume of the charge as melting causes filling of voids. The lower middle of an iron blast furnace is called the "bosh," the point of maximum diameter being regarded as the top of the bosh. The section at the bottom of the furnace is known as the "crucible," and in it collect both the crude molten iron and the slag. The crucible is provided with two openings, the upper one being just above the maximum height the molten metal is allowed to attain, and from it slag is drawn at intervals. The lower one is on a level with the bottom of the crucible, and from it molten metal is tapped. Well above the highest level at which molten slag is allowed to stand are a series of nozzles called "tuyères," through which heated air is blown. At the top of most furnaces are two concentric cones known as "bells," the smaller one being a short distance above the larger. The lower bell, when pulled up as far as it will go, serves to seal the top of the furnace proper, while the smaller upper bell seals a charging compartment. Lowering the upper bell admits the charge to this compartment, and lowering the lower admits it to the furnace. Other methods of feed and distribution are also used. Near the top of the furnace is a duct which carries the blast gas to the heat-recovery and purification system. The furnace is essentially continuous in operation, although the feed and discharge are intermittent. The ore, limestone, and coke are fed in at the top, usually by a skip hoist.

The charge of ore, limestone, and coke is first heated by the waste gases. As the charge moves down, the calcium carbonate decomposes to give calcium oxide and carbon dioxide: $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$. Wherever the temperature is sufficiently high, the carbon dioxide is reduced by heated carbon to form carbon monoxide:



This in turn reduces the oxides of iron. Assuming the oxide is ferric oxide, the reaction is

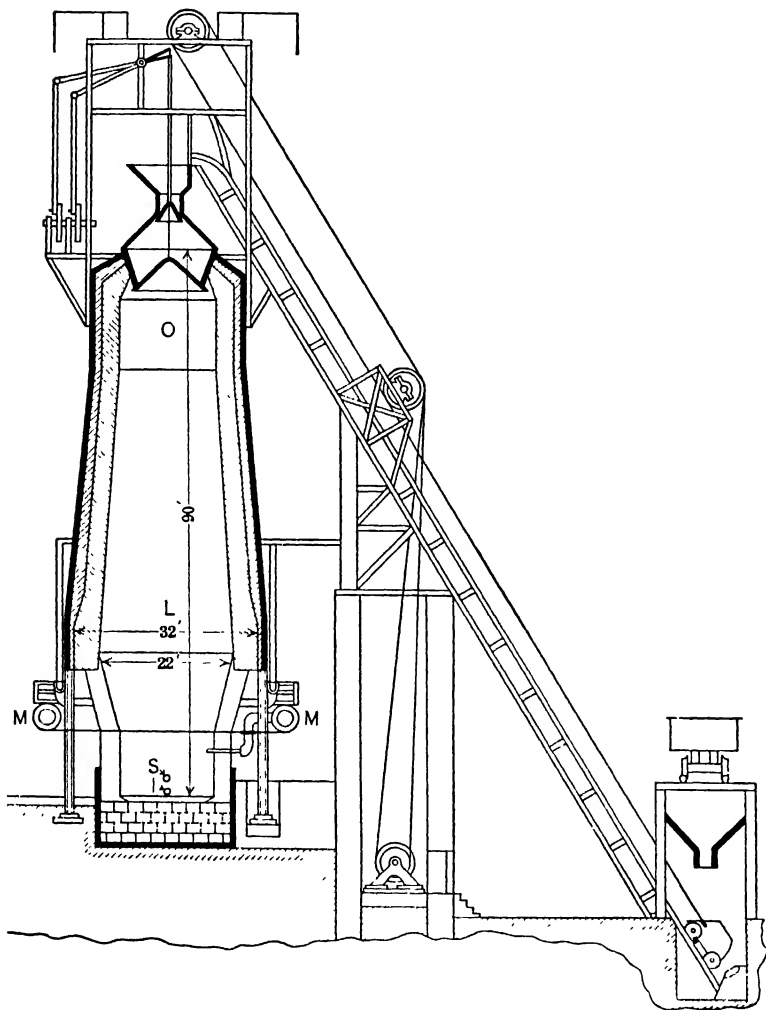
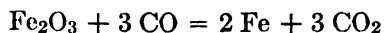
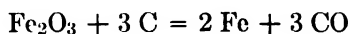


FIG. 89.—Blast Furnace for Iron. From Deming "General Chemistry."

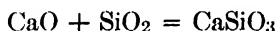
L. Melting Level. M. Air Main. O. Outlet for Gases. S. Tap Holes.

This reduction is probably in steps with the formation of FeO and Fe_3O_4 . Carbon monoxide is always formed when carbon dioxide comes in contact with heated carbon, and at temperatures around 1000°C .

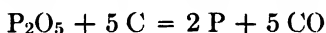
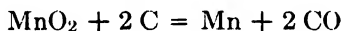
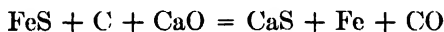
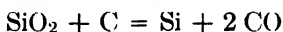
its formation is practically quantitative. Hence, regardless of the height of the furnace, there will always be some carbon monoxide in the exit gases. Some carbon is deposited in the cooler portions of the furnace. Wherever iron oxide comes in contact with carbon, there is reduction:



Since the ore is in lumps, most of the reduction is accomplished by carbon monoxide gas. In the region of the bosh the heat caused by the burning of coke in the blast of heated air is so intense that the reduced iron melts and the silicates of the ore combine with the quicklime in the charge to form a slag. Calling these silicates SiO_2 for purposes of simplification, the reaction may be represented thus:



In the zone in which the charge becomes liquid other reactions take place, of which these are the most important:



The silicon, manganese, and phosphorus dissolve in the metal, and the calcium sulfide goes into the slag. Equilibrium is not reached in all cases, and with so many factors affecting equilibria it is very hard to get a clear picture of what takes place. However, long experience, supplemented by a better understanding of the complicated chemistry of the process, has made possible the continuous and uniformly successful operation of blast furnaces for many years.

The gas from the top of the furnace contains sufficient carbon monoxide to give it some fuel value, around 90 to 100 B.t.u. per cubic foot. About one-half the fuel value of the coke used is in the gas. Dust is removed, and the clean gas is used to preheat the air blast and to furnish power. Preheating is accomplished by burning the gas in a "stove," which is a vertical steel shell filled with firebrick so as to leave a series of vertical flues. After a stove has become quite hot, the gas is sent to other stoves, while air is blown through the flues. The firebrick serves as a heat reservoir. Only about one-third of the gas made by a blast furnace needs to be used for preheating air. The remainder is either burned under steam boilers or used directly in gas

engines. A considerable part of the power derived from this gas is used to blow air into the blast furnace.

Where electric current is very cheap and coke and charcoal costly, the actual reduction of iron ore may be accomplished by an electric furnace, with carbon as a reducing agent. Many "ferro" alloys, used for introducing alloying metals into steel, are made in the electric furnace. Most electric heat, however, is utilized in purification and refining processes.

The slag, which accumulates on top of the molten crude iron, is drawn off several times as often as the metal. Except for certain slags that may be used in making portland cement, this material has no value, and is poured on the slag dump. The metal that is tapped from the crucible may be placed in a great ladle known as a "mixer," which can be tilted to discharge its contents. By reason of the great size of the mixer the iron is kept molten with the use of very little auxiliary heat. If the crude iron is not to be purified immediately, it is cast into "pigs." This was once accomplished by allowing it to flow into a series of connected sand molds, but casting is now more generally done in a series of molds which function as a continuous conveyor.

It is often advantageous to leave in the refined metal small amounts of some substances, but in general practically complete purification and addition of alloying materials may be considered as the basic principle of all processes in which alloys of iron are made.

There are two fundamental methods of purifying the crude iron from the blast furnace: burning out the excess carbon with a blast of air with simultaneous slag formation; and supplying the necessary oxygen in the form of an iron oxide, the oxidized impurities being removed as carbon monoxide and as components of a slag.

Bessemerizing. Converting is known in iron metallurgy as "Bessemerizing" because of the use of the "Bessemer converter." This is a steel shell of approximately oval form, supported at each side to permit tilting and pouring. There is a large opening at the top, and a large number of small openings in the bottom lead down to a common space into which air is admitted. The converter is lined with a thick layer of refractory material, mainly silica. Because of excessive wear, the bottom is removable for replacement. The converter is charged by tilting it on its side and pouring into it some 10 or 15 tons of molten crude iron from the mixer. Air is blown through the holes in the bottom, and the converter is turned back to a vertical position so that the metal is about 18 in. in depth over the bottom. Sparks,

essentially small drops of molten iron and slag, are followed by a flame which ultimately rises to a height of 30 ft. above the molten and violently agitated metal and lasts 8 to 10 minutes. The heat of reaction serves to raise the temperature considerably. The carbon has been reduced to less than 0.1%; most of the other elements have been oxidized and their oxides have combined with the silica formed from the silicon in the metal. The basic Bessemer process, which involves a basic lining and addition of lime, is not used to any extent in this country, since few ores are high in sulfur and phosphorus. In the acid Bessemer process, after the blowing is complete, carbon and other alloying elements are added, those other than carbon usually in the

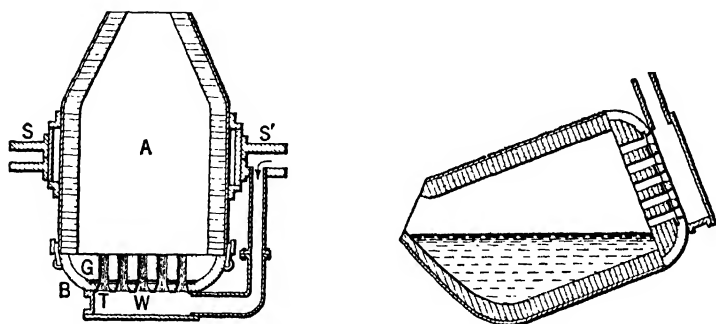


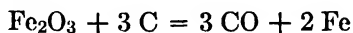
FIG. 90.—Bessemer Converter (Vertical Section and in Inclined Position). From Rosenholtz "Elements of Ferrous Metallurgy."

A. Body of Converter. B. Bottom. G. Refractories. S. S'. Trunnions.
T. Tuyères. W. Wind Box.

form of alloys of iron and the desired element. These are known as "ferro" alloys, of which ferrosilicon, ferrovandium, and ferromanganese are typical. The Bessemer process was responsible for the initial development of the iron industry, but is now of secondary importance except as a preliminary step in open-hearth refining.

Production of Wrought Iron. The removal of carbon to a value of less than 0.1% from the crude iron results in a tough, malleable product that is called "wrought iron." It may be subsequently converted into steel, but a considerable amount is used as such. The process has the disadvantages of small units (three-fourths of a ton) and much hand work, since until recently no mechanical devices have been able to produce wrought iron. The underlying principle of wrought-iron manufacture is to place pig iron in a small reverberatory furnace whose hearth is covered with an iron oxide, and melt these materials by the

heat derived from a long flame from a coal fire. The oxidation of the carbon is by the reaction



The carbon monoxide burns as it escapes and adds to the heat. The silicon and manganese are likewise oxidized fairly completely and form a slag, which is ultimately tapped off at the level of the molten metal. Phosphorus is only partially removed, and sulfur to a still smaller degree. In addition to acting as a source of oxygen, the oxides of iron function as basic oxides in slag formation, ferrous oxide amounting to nearly two-thirds of the total slag. The melting point of the metal increases as impurities are removed until ultimately it becomes quite pasty and thick. The iron is collected on heavy rods suspended by chains until balls of around 100 lb. in weight can be removed. Each ball is rolled in a squeezer so that the bulk of occluded slag is removed from its surface. Some slag remains in long filaments in the metal, and wrought iron may be identified by this structure. A promising process developed by Aston for the production of wrought iron in a mechanical furnace consists in pouring "fully blown" Bessemer metal into a liquid slag. Small globules of metal are formed, each covered with slag. These globules cling together to form a ball, which is squeezed to remove the slag, and the metal is later rolled. The product is said to compare most favorably with hand-puddled wrought iron.

Crucible steel, from which the finest of tempered articles are made, results from the melting of wrought iron in small amounts in graphite-fireclay crucibles with the addition of the requisite amount of carbon.

Open-Hearth Methods. The process most largely used for purification of pig iron for the production of steel is known as the "open-hearth" or "Siemens-Martin" process. This process resembles in principle that used in making wrought iron in that reverberatory furnaces are used and oxygen is derived from iron oxide. It differs, however, in so many important ways that the two should not be confused. An open-hearth furnace has a capacity of from 50 to 350 tons of final product. The greater depth of metal on the hearth means much slower operation. Gas, oil, tar, and powdered coal are used as fuels. To prevent melting of even the most refractory materials the gases are not allowed to strike the roof, neither are they deflected on to the surface of the metal, but burn between the two. The common material for lining the hearth is magnesium oxide. When this is used as a lining, the process is known as "basic open hearth." Siliceous

linings are used where the bulk of the charge is steel scrap and the pig iron is very low in phosphorus and sulfur. The lining takes no part in the reactions. The oxidizing agent in the open-hearth process is an oxide of iron, either ore high in ferric oxide or mill scale, which is magnetic oxide of iron, Fe_3O_4 . Large quantities of this result from the oxidation of iron at high temperatures in mechanical processing. An open-hearth furnace may be as much as 60 ft. long, the hearth itself being 40 ft. long and about one-half as wide. The gas and preheated air are admitted separately through a series of openings or ports at one end of the furnace, and the hot gases escape through similar ports at

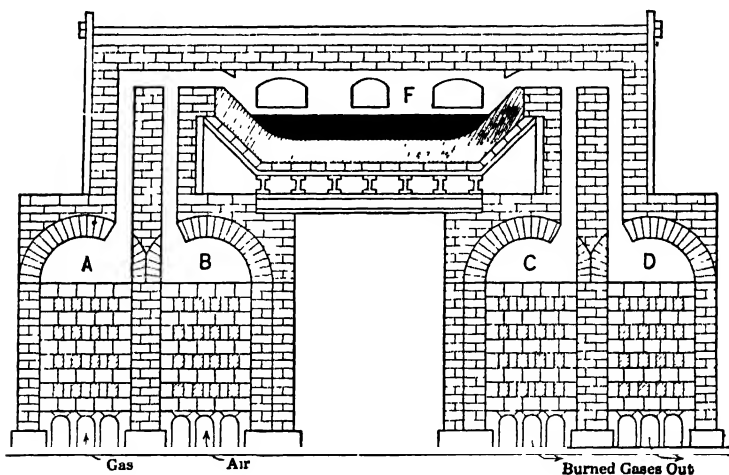


FIG. 91.—Open-Hearth Furnace. From Deming "General Chemistry."

A. Gas Regenerator. B. Air Regenerator. C. and D. Burned Gases out over Regenerators. F. Furnace.

the other end. Heat exchange and recovery are accomplished by checker brick regenerators, the flow of air and gas and that of waste gases being reversed at frequent intervals. The great heat of the escaping gases necessitates water-cooling the ports, and in spite of this precaution the wear on these is very great. Carefully regulated mechanical draft is employed. The bottom of the furnace is first covered with scrap steel, preferably in the form of thin plates. Above this are limestone and ore or scale. The hearth is then filled with scrap steel and pig iron, with the former predominating in amount. When the charge has settled because of softening after a period of heating, more pig iron is added and some scrap steel. Molten crude iron from a mixer may be used, but only as a part of the charge, and

it is added after melting has begun. Carbon, silicon, phosphorus, and manganese are oxidized and removed, carbon as carbon monoxide, and the others as a slag or glass. The removal of sulfur in this process is only partial and unreliable. The iron oxide dissolves in the slag and the reactions take place in the liquid phase. The slag floats on the surface of the metal and prevents surface oxidation. However, the escape of carbon monoxide stirs the metal and causes sufficient mixing to bring about removal of impurities by the iron oxide. Since carbon is the last element to be removed, its amount may be controlled without leaving undesirable elements in the metal. In general, however, the open-hearth process should be considered as one of refining. The slag is a glass of complex composition; it contains calcium, magnesium, and ferrous oxides as bases, and silica and phosphorus pentoxide as acids. Manganese first forms a sulfide, which floats to the surface where the sulfur is oxidized, and manganese returns to the metal. At the end of the operation the tap hole, located at the bottom and towards one end of the furnace, is opened by means of a bar until metal is reached. There will be some red hot but solid metal on the bottom, and a hole is burned in this by a current of oxygen. As the molten metal runs from the furnace the necessary alloying materials are added, these being carbon and various alloys of iron such as ferro-silicon, ferromanganese, and ferrophosphorus.

The "duplex" process is a combination of the Bessemer and the open-hearth processes. The major portion of the purification of the product of the blast furnace is accomplished very rapidly by blowing air through the metal in a Bessemer converter, practically all the silicon and manganese being removed together with most of the carbon. The product of the Bessemer is placed in a mixer and subsequently run in an open-hearth furnace for further removal of carbon and phosphorus.

Electric Furnace Methods. The use of the electric current in the metallurgy of iron has greatly increased in recent years. Electric heat accomplishes all that can be done in small units in crucibles. The primary purpose of an electric furnace is to refine to a high degree of purity a metal that has been refined as far as profitable in the open-hearth process. Both arc and induction furnaces are used. Electric "super-refining" includes adding, to molten open-hearth steel, lime, fluorspar, and sand to make a slag, and when both slag and the surface crust of metal are melted, putting in coke dust. The heat of an arc furnace is sufficient to cause the formation of calcium carbide, and this serves to reduce sulfides and oxides of iron and manganese to free metal. In the induction furnace no carbide is formed and carbon is

the reducing agent. Carbon monoxide escapes and calcium sulfide remains in the slag. Gases are completely removed at the same time. Alloying materials and deoxidizing agents are added early in the process as "ferro" alloys. By providing for a "quiet" period of an hour in the furnace and then tapping electric steel below the surface of the slag, the presence of occluded oxides known as "sonims" may be completely avoided.

Electrolytic Methods. Very pure iron can be made by electrolytic deposition. As long as the metal contains occluded hydrogen it is very brittle. This very property is taken advantage of in making magnet cores, in which the hard particles resist being pressed together until shaping operations are complete, thereby insuring high resistance. Hydrogen is subsequently removed by baking. Tubes of electrolytic iron, which have been formed by deposition on a mandrel and which have subsequently been annealed, are beginning to find use in steam boilers. A great deal is being done and much yet remains to be done with very pure iron.

COPPER

Because of its high electrical conductivity, malleability, ductility, and resistance to atmospheric corrosion, copper is a very valuable and necessary metal. It is also extensively used in alloys, the best known being brass and bronze. The production of copper in the United States in 1929 was 894,000 tons, valued at \$352,000,000. Copper occurs as free metal, and in combination with other elements, chiefly as sulfide, oxide, carbonate, and silicate. It is also present in double sulfides with iron and arsenic. In most cases, ores contain gold and silver, which are recovered as by-products. Copper ores containing a relatively high percentage of copper are rare, the average in the United States for 1925 being 1.6%. Modern methods have made it profitable to extract copper from ores containing as low as 0.5% copper, but it is necessary to employ concentration methods, both gravity settling and flotation.*

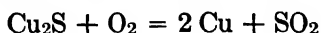
Copper ores are increasingly handled by hydrometallurgical methods. Many concentrates must be roasted to produce cupric oxide from other copper compounds before sulfuric acid leaching. Ores containing cuprous sulfide are leached with ferric sulfate solutions containing free sulfuric acid. Ammoniacal solutions, most commonly ammonium carbonate, will dissolve copper, both free and in compounds, but such reagents are expensive, and ammonia must be recovered by heating the solutions. Copper is recovered from sulfate solutions either by the

action of iron, or more commonly by electrolytic deposition with the use of insoluble anodes.

Pyrometallurgical methods are still more common than hydrometallurgical in the copper industry, although the latter are increasing in importance with ores of lower grade. Copper is first obtained in the form of a mixture of cuprous sulfide and ferrous sulfide called "matte." If the ores that come to the smelter are all sulfides, they are roasted to reduce the sulfur content to the required amount. If oxide ores are available, the sulfur content is regulated by adding these to sulfide ores.

The roasting of sulfide ores is accomplished in multiple-hearth furnaces or in special sintering furnaces if the ore is to be handled in a blast furnace. The object of roasting is the lowering of the sulfide content, and not complete oxidation. A blast furnace for copper differs considerably from a blast furnace for iron, using no preheated air, operating at a lower temperature, and being rectangular in cross section with a maximum width of 4 ft., and a length corresponding to capacity. Where the charge is high in sulfur, very little fuel is required, the burning of the sulfur in the presence of excess oxygen giving the necessary heat. This is known as "pyrite smelting." At the other extreme are charges relatively low in sulfur, where considerable amounts of fuel are used. The matte and slag are continuously drawn from the furnace into a reservoir or "settler" from which the slag overflows and the matte is tapped. Blast furnaces are being rapidly supplanted by reverberatory furnaces. These are better adapted to handling finely divided roasted concentrates. The charge is admitted to the furnace through the upper part of the side walls near the firing end. Fuel oil and powdered coal are most commonly used as fuels. The waste gases pass through waste heat boilers on their way to the stack. In the larger furnaces, the slag runs off continuously at the end away from the fire, and the matte is tapped at intervals.

The molten matte is conveyed by ladles to converters. The principle is somewhat the same as a Bessemer, but differs in that the process is much slower and the air blows in at the side, so that copper collects at the bottom, while the blast passes continuously through matte. Material containing silica, usually an ore, is added at first to form a slag with the ferrous oxide. Iron sulfide decomposes first, and when the iron has been oxidized to ferrous oxide and absorbed in the slag, the converter is tilted and the slag is poured off. Cuprous sulfide is then converted to copper by the removal of sulfur, thus:



The metal produced is around 99% copper, and is known as "blister" copper, because of the appearance of the surface of the cast pigs from which sulfur dioxide has escaped during solidification. The modern type of converter is a horizontal cylinder lined with magnesite brick, equipped on the side with a large number of tuyères, and provided with tires and girth gear for tilting. In order to avoid excessive wear and corrosion, the temperature is kept below 1200° C.

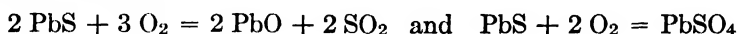
Since blister copper contains some impurities that may seriously interfere with electrolytic refining, it is often necessary to subject the metal to another refining operation before casting it into anodes. The increase in copper content is not large, but those impurities are removed which would contaminate the electrolytic bath or prevent proper casting of anodes. Molten copper from the converter is poured into a reverberatory furnace and air is blown through the metal to oxidize some of the impurities to a slag, but no flux is added. The slag is skimmed off. Some copper is oxidized to cuprous oxide, which is capable of dissolving in molten copper up to about 6%, and this oxide must be reduced. Young trees are stripped free of branches and placed in the molten metal. Steam and gases serve to bring about thorough stirring, and the carbon and carbon compounds reduce the cuprous oxide to copper. The process is known as "poling." The metal is then cast by special machines into slabs with projections at the upper corners, and these function as anodes in the subsequent electrolytic refining operations. The process of refining copper by electrolytic deposition has been discussed in another chapter. The copper cathodes from the electrolytic refining process are melted, cuprous oxide is removed by poling, and the metal is cast into shapes required by subsequent fabrication operations. The most valuable components of the slimes from the refinery tanks are gold and silver. Unless the original ore contains as much as 20 oz. of silver per ton, it is more profitable to refine the copper by furnace methods. Native copper is handled by concentration, smelting the concentrates with a limestone flux, and refining by means of a furnace.

LEAD

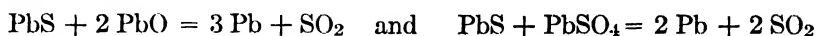
Except for some recent promising developments in chloridizing and sulfatizing processes followed by extraction with a strong brine, all lead is obtained from concentrates by pyrometallurgical methods. The only important compound of lead from which the metal is obtained is galena or lead sulfide, PbS . The method of treatment of the ore depends very largely on the amount of silver present as well as the

amount of silica in the material obtained by gravity concentration. For those ores low in silver, and with not more than 5% silica, ore-hearth smelting is the common process. Coke in relatively small amounts is mixed with the ore and functions both as a fuel and as a reducing agent. In addition there are the so-called "roast reactions."

Lower temperature:



Higher temperature:



There is no effort to operate at two distinct stages. There is no slag, and the molten lead is drawn off when it reaches a certain level in the hearth. The product is a high grade of lead. The process would cause an excessive volatilization of silver.

The most common process for obtaining lead from lead sulfide ores is by the use of the blast furnace. The ore must be subjected to a preliminary roasting for the removal of a part of the sulfur. The object of roasting is to reduce the sulfur to a maximum content of 3%. The material fed to a lead blast furnace may be of relatively low lead content with a substantial amount of impurities, and the process is particularly adapted to those ores carrying considerable silver. Both crude free metal and a matte are formed. The matte contains the copper of the ore, and is sent to a copper furnace. The lead blast furnace resembles a copper blast furnace in being rectangular in cross section and quite narrow in comparison with height and length, and it is necessary that the air from the tuyères should penetrate to the center of the furnace. Instead of continuous removal of both slag and metal, a lead blast furnace is provided with collecting space from which the lead is removed by means of a siphon device, while slag and matte are tapped from an opening above the metal and subsequently separated. Most of the gold and silver remain in the metal. The product of the blast furnace contains from 96% to 99% lead.

Crude lead may be refined by an electrolytic process, which yields extremely pure lead. Unless current is very cheap or bismuth is present in paying amounts in the crude lead, electrolytic refining is not profitable, and fire processes are most commonly used. It is necessary first to subject the lead to "softening" in a reverberatory furnace. Tin, antimony, and arsenic are removed by oxidizing these elements and skimming their oxides from the molten lead as a dross, this being accelerated by additions of litharge. Copper is not affected, but may

be previously removed by melting the lead and allowing it to stand at a temperature slightly above its melting point. Copper rises as a scum, and its separation may be facilitated by adding sulfur and removing the copper sulfide formed. Still another softening method is to oxidize the impurities with small amounts of sodium nitrate in the presence of molten caustic soda, in which the oxidized substances dissolve as arsenates, antimonates, and stannates. The lead still contains gold, silver, and bismuth. There are two methods of preparing high-grade lead. The Pattinson process consists of repeated fractional crystallization, with the removal of pure lead and the accumulation of gold, silver, and bismuth in the liquid phase. The Parkes process is more generally used; it is based on the formation of an alloy of zinc, silver, and lead, the small amount of gold functioning in the same way as silver. The crude lead is maintained at a temperature considerably higher than its melting point, and zinc is added. The alloy rises to the top and is skimmed off continuously until desilverization is complete. The molten metal contains some zinc, which is later removed by being oxidized in a furnace, the zinc oxide being skimmed from the surface. Bismuth is not removed by this process, but is usually not present in sufficient amounts to affect the quality of the lead. Gold and silver are isolated from the alloy by distilling off the zinc and removing lead by oxidizing it to litharge which flows from the surface of the molten precious metals.

ZINC

The zinc industry is divided into the manufacture of zinc metal and zinc pigments. The latter are discussed in Chapter XXVII on Paints and Varnishes. The largest single use of zinc metal is as a protective coating for iron, the metal being applied by the process known as galvanizing. Following are the uses of slab zinc in the United States in 1930.

	TONS
Galvanizing	217,000
Brass making	145,000
Sheet zinc	51,400
Die castings	21,500
Other Uses	41,000
	475,900

A very important use of zinc that has been developed in recent years is in die casting. The cast metal contains of the order of 93%

zinc, and is used very generally where the physical and chemical properties of such alloys render them suitable. Such materials have high tensile strength (45,000 lb.), and are commonly employed in the automobile and hardware industries.

The average amount of zinc in brass is 30%.

One of the most important uses of sheet zinc is in the production of battery cups used in dry cells.

The two most important zinc ores are the sulfide and the oxidized ores. The sulfide is known as zinc blende; the principal oxidized minerals are smithsonite and calamine. The ores as found vary widely in zinc content, but those low in zinc sulfide are concentrated by gravity and flotation. Most zinc metal is obtained by pyrometallurgical methods, but the electrolytic method is used at some plants. As a preparation for any process of extraction, sulfide ores must be roasted. Oxidized ores can be handled directly.

Zinc sulfide roasting requires very careful control, since that compound must be completely broken up for further treatment or reduction. A portion of the zinc goes into the form of a sulfate, but the bulk of it is converted to zinc oxide. At higher temperatures, conversion to the oxide is complete. By the use of muffle furnaces in which the products of combustion are not mixed with the gases from the oxidation of zinc sulfide, it is possible to obtain sulfur dioxide in sufficient concentration to use in sulfuric acid plants.

In producing zinc by the electrolytic process the roasted ore may be extracted with dilute sulfuric acid, and the resulting zinc sulfate solution, after removal of undesirable substances, is electrolyzed with insoluble anodes with the deposition of very pure zinc.

However, more than four-fifths of all metallic zinc is produced by pyrometallurgical methods. These in the main consist of reduction of zinc oxide with carbon, and distillation of the reduced zinc. The zinc sulfate present breaks down first into zinc oxide and sulfur trioxide.

The old-fashioned process, which has gone essentially unchanged for a century, employs small, horizontal, clay retorts resembling somewhat the "stop end" retorts of the early coal-gas industry. The retorts are usually cylindrical or elliptical, and are slightly inclined downward towards the open end. They are arranged in blocks, and these in turn are in pairs back to back. At the end of each retort is a short fireclay pipe serving as a condenser, with a bulge on the lower side for a receiver. Attached to this is a sheet-iron cylinder terminating in a cone, in the end of which is an orifice to permit escape of carbon monoxide, which burns when it reaches the air. The retorts are charged

with a mixture of ore and coal or coke, the fuel being several times in excess of theoretical for reduction. General practice is to draw the metal three or four times during the twenty-four hour run, the first distillate being the purest. In this operation losses of 10% to 15% are always observed.

The most advanced form of production by pyrometallurgical means uses large vertical retorts, which are continuously charged and discharged, and in which zinc of the highest purity is produced.

ALUMINUM

The production and refining of aluminum have been described as electrochemical operations. Aluminum is the most abundant of all metallic elements, but a very considerable part of it is in the form of complex silicates from which the metal is not profitably obtainable by present processes. It is estimated that the world's supply of bauxite, a hydrated aluminum oxide, is sufficient to meet the present yearly demands for a raw material for the production of metallic aluminum for some fifteen centuries. The growth of the aluminum industry, however, has been phenomenally rapid, and new uses are being continually found for the metal and its alloys. The production of aluminum in the United States is of the order of 200,000 tons per year. The product of the electrolytic process is from 99.0% to 99.4% pure, and only a very small part of this is refined to a higher degree of purity. It is estimated that around one-half of the metal is used without further alloying.

The resistance of aluminum to corrosion is due to the formation of a thin and closely adhering film of oxide, which protects the metal against ordinary corrosion conditions. The very low specific gravity of aluminum and the fact that it may be alloyed with small amounts of other metals in such a way that it has the properties associated with mild steel make it very valuable for uses where weight is a major consideration. The electrical conductivity of aluminum is about 0.6 that of copper, but because of its low specific gravity, it competes successfully on a weight basis with copper in the transmission of electricity. Some 500,000 miles of aluminum cable in electric power lines are now in use. The conducting cables are reinforced by galvanized steel cores. The commercial metal is readily rolled, extruded, or drawn. Its alloys can be cast or forged, the method used depending on their composition. Certain alloys can be given more desirable properties by heat treatment. Cold rolling serves to elongate and otherwise deform the crystals until the metal becomes quite hard. The

annealing process, or heating to a temperature well below the melting point, serves to relieve these strains and restore the properties of softness, ductility, and malleability.

A number of very valuable aluminum alloys have the disadvantage of being subject to corrosion. This has been overcome by coating them with a thin layer of relatively pure aluminum. The most satisfactory method of securing this coating is to line the ingot molds, which receive the molten alloy, with thin sheets of aluminum. There is partial melting and diffusion and a gradual progression in the amount of aluminum, until the outer layers contain no alloying metals. The protection is both that of a covering and a galvanic effect of the same nature as zinc on iron.

The uses of aluminum and its alloys in chemical industry have been discussed under "Materials of Construction." Aluminum is extensively used as a structural material in buildings, machinery, and particularly in the automobile and aeronautical industries. Cooking utensils represent a very substantial use. Aluminum is a deoxidizer in the steel industry along with ferrosilicon and ferromanganese. Powdered aluminum is a powerful reducing agent, and may be employed in obtaining chromium from chromium trioxide, and particularly with ferric oxide in the process of "thermit" welding. Along with ammonium nitrate it functions as a component of the explosive "ammonal." In addition to its use as a protective coating of other alloys, aluminum serves to produce a highly resistant surface by the process of heating metals in the presence of powdered aluminum, the surface being penetrated by this material much after the fashion of zinc in the sherardizing process. Aluminum paint is valuable not only because of its chemical resistivity and its flake structure, but also its ability to reflect radiant heat, being used to prevent both heat losses from furnaces and heat absorption by transformers, tanks, and tank cars.

OTHER METALS

The principles underlying the production of these common and widely used metals also characterize other metallurgical processes. The metallurgy of *gold* and *silver* differs mainly in that most ores contain so little of the metals that it is necessary to remove them by means of chemical reactions even after concentration has been used to the limit of its efficiency. Mercury is used to dissolve gold and silver with the formation of an amalgam. Alkali cyanides are the most common reagents for extraction from concentrates, their effectiveness being due to the formation of very stable complex cyanide ions. Con-

siderable amounts of gold and silver are recovered in the refining of copper, and silver is very often found along with lead. The electrolytic refining of gold yields enough *platinum*, *palladium*, and other precious and rare metals to pay for the process. *Mercury* differs from other metals in its resistance to oxidation, low boiling point, and the ease of reduction of its oxides, so that reduction and distillation may be carried out in a single operation.

ALLOYS

Stoughton gives the following as the definition of alloys on which metallurgical authorities agree: "A metallic alloy is a substance possessing the general physical properties of a metal, but consisting of two or more metals, or of metals with non-metallic bodies in intimate mixture, solution, or combination with one another, forming, when melted, a homogeneous fluid." The whole field of physical metallurgy has to do not only with the internal structure of pure metals, but to a much larger extent with the structure, composition, and equilibria of alloys. Since all alloys result from homogeneous melted materials, it is necessary that a study of alloys must be based on modern conceptions of solutions and the equilibria between various liquid and solid phases.

All alloys may be divided broadly into two classes, homogeneous and heterogeneous. A homogeneous material is alike in physical properties so that samples taken at any points and subjected to the most rigorous examination will show no differences. Heterogeneous materials are made up of two or more substances which may be separated by physical means so that each can be proved under examination to have different physical and chemical properties, and whose phases are entirely distinct from each other. A heterogeneous material is represented by crystals in the presence of a saturated solution, by suspensions and emulsions, and by mixtures of particles.

Homogeneous Alloys. Although there are some very useful and valuable alloys of the homogeneous class, they are of less common occurrence and less commercial importance than heterogeneous alloys. True chemical compounds between two or more metals are not extremely common, but a number are known. As examples may be cited a tin-magnesium compound, SnMg_2 , and such compounds of copper as are represented by the formulas Cu_2Zn_3 , Cu_3Sn , and CuAl_2 .

A more common type of homogeneous alloy is a solid solution. In this the atoms of one element may take the place of another in the space lattice of the crystal, which means that they must have the same

internal crystalline structure as revealed by X-ray examination. Gold and silver form such stable solid solutions.

Supercooled liquids represent a state of metastable equilibrium, and represent mixtures which would produce a heterogeneous material under another set of conditions.

Heterogeneous Alloys. A mixture of crystals of two or more kinds constitutes a heterogeneous alloy. These crystals may be practically pure substances, either metals or compounds of metals, or they may be solid solutions containing varying but small amounts of other elements. When a liquid or molten mixture of two substances deposits crystals of each substance, the liquid of that composition is known as the "eutectic" solution, and the temperature at which simultaneous crystallization takes place is the "eutectic" temperature. This temperature is lower than the melting point of either component, and lower than any other temperature at which there is equilibrium between a solid and liquid phase. The simpler type of a homogeneous alloy behaves exactly in the same way as the aqueous solution of ordinary salt. Antimony and lead form a eutectic containing 13% antimony and 87% lead with a eutectic temperature of 246°C . Antimony melts at 630°C . and lead at 326°C . If a molten mixture of these two metals containing more than 87% lead is cooled, lead will crystallize practically free from antimony, and the temperature will drop until the eutectic point is reached. Then both antimony and lead crystals of very small size will deposit in a sort of banded or striated structure. If the mixture contains more than 13% antimony, on cooling, antimony crystals will deposit until the eutectic is reached. Owing to its structure of fine and thoroughly intermingled crystals, a eutectic has greater tensile strength than an alloy of any other composition. Obviously any other alloy will be made up of relatively large crystals of the predominating component and some eutectic, the amounts of each being determined by the original composition of the molten mass.

When more than two metals are present the equilibria are more complex. Alloys of three or four metals are known whose melting point is not far above room temperature. A three-component mixture is represented by triangular coordinates, so that when temperature is represented by vertical height, the whole system requires a solid model. Peaks indicate the melting points of pure components, valleys equilibria between two components, and lake beds without outlets are ternary eutectics.

The situation becomes more complex where the two crystals that

form at the same time are each solid solutions or chemical compounds, or where one is a solid solution and the other a chemical compound. In the copper-zinc system, alloys containing more than 64% copper are known as "alpha brass" and are solid solutions. When the copper drops to 64% there appears another solid solution known as "beta brass," which is both harder and more brittle. When the copper is 39% of the mixture and zinc 61%, there is formed a compound, $\text{Cu}_2\text{Zn}_{11}$, known as the "gamma" component, which is a very brittle material. The copper-tin diagrams are still more complex, but only those alloys containing 88% or more of copper are of commercial importance, and in these only one solid solution is present.

There are a very large number of alloys of aluminum with a variety of metals. The product known as "duralumin" may be selected as typical of a variety of alloys that have the same general properties as steel. This alloy has around 4% copper and 0.5% each of magnesium and manganese. Considering the effect of copper alone, it should be noted that copper and aluminum form a compound, CuAl_2 , which is capable of existing in solid solution at higher temperatures. If an alloy of this type is cooled slowly, crystals of this compound separate from the solid solution until at room temperature very little copper remains dissolved. If it is cooled very quickly, a metastable condition results, and it requires several days for separation of crystals, which are very small. When this alloy is heat treated and quenched suddenly, the material has a tensile strength at first of about 45,000 lb. per square inch. After several days this value rises to 60,000 lb. Other alloys give better results if kept warm during the "aging" period. The strength and hardness of such alloys are believed to be due to the effect of the space lattices of the crystals of CuAl_2 , which tend to prevent slipping under strain. When the material is soft and ductile, these crystals are of the order of 1×10^{-4} in. in diameter, and when it is quite hard, they are not more than 1×10^{-6} in.

The alloys of iron are more widely used than those of any other metal. The element most generally present in iron alloys is carbon. It is the main impurity of cast iron, and, as shown earlier in the chapter, a considerable part of the metallurgy of iron is concerned with its removal. However, it confers certain properties on iron which make its presence in limited amounts highly necessary and desirable. A number of alloys of iron with such elements as nickel, chromium, vanadium, molybdenum, manganese, tungsten, and silicon, meet certain requirements which an iron-carbon alloy will not. Even the more complex alloys of iron contain some carbon. Since the field of iron

alloys is too broad to take up even in outline, attention will be confined to the carbon-iron system.

Pure iron is known in three allotropic modifications, alpha, beta, and gamma ferrite. Only the alpha variety is stable at ordinary temperatures, and for purposes of simplification only this variety will be considered except in connection with hardening. At high temperatures the system of iron and carbon resembles to a considerable extent the antimony-lead system, but is more complex in that neither pure carbon

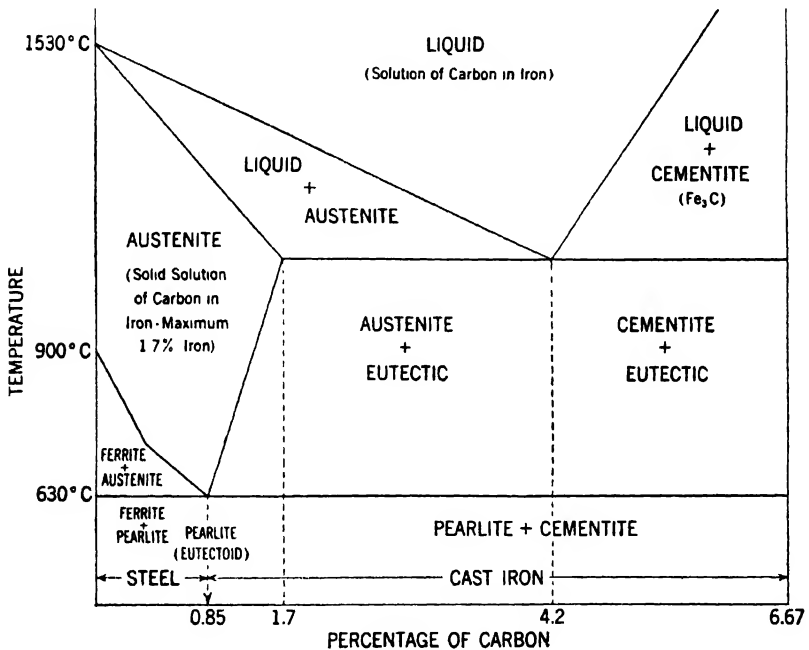


Fig. 92.—Iron-Carbon Diagram.

or pure iron separates from the molten mass. When iron separates from a liquid composed of iron and carbon, the solid carries with it considerable carbon. If the amount of carbon in the original melt is less than 4.2%, the iron will contain carbon in it as a solid solution, which is stable down to 1135° C. If the carbon is greater than 4.2%, the crystals that separate are iron carbide, the formula usually assigned to this substance being Fe₃C. Since crude iron rarely has more than 5% carbon and usually less, not so much attention needs to be directed to very high-carbon alloys.

At 1135° C. the maximum amount of carbon that can remain in

solid solution is 1.7%. If the amount of carbon is 1.7% or less, no iron carbide will form, and the crystals will be solid solutions of carbon in iron. If the amount of carbon is less than 4.2% but greater than 1.7%, the crystals that separate will be a saturated solution of carbon in iron of 1.7% carbon content. As this forms, the liquid will become richer in carbon and poorer in iron until the value of 4.2% is reached. This is the eutectic point in the liquid-solid equilibrium range, and fine crystals of two kinds separate together, one being the same 1.7% solid solution of carbon in iron, and the other iron carbide, Fe_3C . Molten iron containing 4.2% carbon remains liquid down to 1135°C ., which is the eutectic temperature. At this point the eutectic of fine crystals separates, the carbon distributed between the saturated solid solution, which is known as "austenite," and iron carbide, which is called "cementite."

As the mass of crystals formed under any of the above conditions cools, the solid solution of carbon in iron containing a maximum of 1.7% carbon undergoes decomposition. If the solid solution is a saturated one, that is 1.7% carbon, decomposition begins immediately at 1135°C . If it has less carbon, the decomposition is at a lower temperature down to 0.85% carbon, where the temperature of decomposition is 690°C . If there is less carbon than 0.85%, decomposition is at a higher temperature than 690°C ., the value being around 900°C . for a trace of carbon, and decreasing with increase of carbon to 690°C . for 0.85%. Thus 690°C . represents the same sort of a point for a solid solution that the eutectic point represents for a liquid, or the lowest point at which a solution can remain in equilibrium with a solute. The solid solution of iron decomposes into crystals of pure iron, or "alpha ferrite," and crystals of iron carbide, or cementite.

If the amount of carbon is less than 0.85%, alpha ferrite crystallizes first, and those crystals are fairly large. The remaining solid solution, just as in the case of ice separating from potassium chloride solution, grows richer in the dissolved material, which in this case is carbon.* When enough iron has been removed to leave 0.85% carbon in solution, and the temperature of 690°C . has been reached, iron carbide separates in fine crystals along with alpha ferrite, whose crystals are also fine. This mixture of fine crystals of cementite and alpha ferrite is exactly the same sort of a mixture as the eutectic from a liquid, and is called in the iron industry a "eutectoid." This mixture bears the technical name "pearlite," because of its flaky, shining structure, resembling mother of pearl.

When the carbon is higher than 0.85% but not more than 1.7%, or

the limit of saturation of carbon in iron, what separates on cooling is iron carbide. As the carbon is removed, the solution grows poorer in carbon and richer in iron until the value of 0.85% is reached, which also means that the temperature of 690° C. is reached, the same thing takes place as just described, namely the precipitation of iron and iron carbide together as the eutectoid, pearlite. The fact that the original molten mixture may have contained more than 1.7% carbon has no bearing on what is taking place on cooling below 1135° C. Any carbon above 1.7% will be represented by iron carbide. If the amount was less than 4.2%, the carbide will be in fine crystals, which separated along with the solid solution, austenite. If the amount was more than 4.2%, which is not often the case, some of the carbide crystals will be larger, since the eutectic of solid solution and carbide did not form until a value of 4.2% carbon in the liquid was reached.

Regardless of the form of the carbide and its amount, we are now interested solely in what becomes of the solid solution of 1.7% or less. It has been shown that when molten iron containing carbon in any amount in which it will dissolve and containing no other elements but carbon is cooled slowly so as to permit equilibrium conditions to be attained until a temperature of around 20° C. is reached, it will be composed of just two things, crystals of pure iron and crystals of iron carbide. The form of these crystals will obviously depend on the original amount of carbon. If that was originally less than 0.85%, there will be coarse iron crystals, fine iron crystals, and fine crystals of iron carbide. If the carbon was above 0.85%, all the iron crystals will be fine and the carbon crystals both coarse and fine.

For purposes of classification all iron-carbon alloys containing 0.85% or less of carbon may be called steel, and all above 0.85% may be known as cast iron. In the iron industry no such ideal conditions obtain, but there must be a thorough understanding of what takes place in the iron-carbon system when there is equilibrium at various temperatures and with various proportions of the two components before the effect of other materials and conditions can be considered.

Commercial cast iron does not consist solely of crystals of pure iron and iron carbide, but there is always some graphite present. Its formation is due to the effect of other elements, primarily silicon. If the silicon is as high as 2.5% to 3%, practically all of the iron carbide is decomposed, so that the cast iron is made up of crystals of iron and flakes of graphite. However, silicon in amounts above 3% has the opposite effect, causing the carbon to be present as iron carbide. Sulfur has a much greater influence on the form of carbon that separates,

causing the crystallization of iron carbide and interfering with the formation of graphite. Ordinary steel, on the other hand, contains so little in the way of elements other than carbon that slow cooling results in a mixture of crystals of iron and iron carbide. The effects of impurities in steel are mechanical rather than chemical. Just as the eutectic from a binary mixture like tin and lead has a greater tensile strength than any other proportion of the two metals, so the eutectoid of iron and iron carbide formed by the decomposition of a solid solution of carbon in iron which contains 0.85% carbon has greater tensile strength than any other of the iron-carbon alloys. Steel made up entirely of this eutectoid is known as "pearlitic" steel. The following table * from Stoughton's "Metallurgy of Iron and Steel" shows the effect of varying amounts of carbon on the properties of the iron-carbon alloys.

CLASSIFICATION	CARBON, PER CENT	TENSILE STRENGTH	
		Ultimate, lb. per sq. inch	Elastic limit, lb. per sq. inch
Very mild steel	0.05-0.15	40,000-48,000	24,000-30,000
Mild steel	0.15-0.25	48,000-60,000	30,000-36,000
Low-carbon steel	0.25-0.40	60,000-70,000	36,000-40,000
Medium carbon steel	0.40-0.60	70,000-80,000	40,000-48,000
Higher-carbon steel	0.60-0.70	80,000-94,000	48,000-56,000
Spring steel	0.70-0.80	94,000-108,000	56,000-64,000
Pearlitic steel	0.85	120,000	70,000

In addition to carbon, most ordinary steels contain some manganese, sulfur, phosphorus, and silicon, as well as traces of oxygen, nitrogen, and hydrogen. Manganese forms a carbide which has very much the same properties as cementite, or iron carbide. All sulfur present combines with manganese if the latter element is present in an amount greater than that required to form manganous sulfide, MnS . If the manganese is less than that theoretically necessary to form this compound, none of it will form and the sulfur combines with iron. The difference between these two sulfides is one of capillarity. Manganese sulfide will coagulate, but iron sulfide spreads out into plates making planes of weakness and brittleness. Hence it is desirable to have several times as much manganese present as there is sulfur. Phosphorus forms with iron a phosphide, and this produces a eutectic with iron which is quite brittle. Carbon serves to accelerate the formation

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of this eutectic. Another effect of phosphorus is to cause the formation of coarse crystals. Hence phosphorus is excluded as far as possible from steels, particularly those which must stand sudden shocks. Silicon has very little effect in the amounts ordinarily present, being mainly beneficial in increasing hardness as well as soundness. Oxygen is extremely harmful, producing carbon monoxide and oxides of iron, all of which render the steel brittle. It is removed as far as possible by deoxidizing agents. Hydrogen is present in very small amounts, and this is true of nitrogen except in arc-welded metal, in which it may be present as an iron nitride, and is a cause of brittleness.

The iron-carbon alloys may be given certain desirable properties by application of the principles underlying solutions, and also by mechanical treatment such as rolling, hammering, and drawing, which tend to modify the shape and arrangement of crystals. Such operations as hardening, annealing, and tempering are carried out without changing the chemical composition of the whole mass, and depend on formation of supercooled solutions and partially arrested equilibria. Case hardening, on the other hand, involves the addition of carbon to the outer surface to produce an alloy of different composition from that of the interior.

White cast iron may be rendered malleable by reheating to temperatures considerably below those at which a liquid would form, and maintaining this temperature for periods of two or three days. During this time graphite separates from the supercooled solid solution, not in flakes as when cooling is slow, but in a fine powder called "temper carbon." Thus the material is stronger and less brittle than cast iron. Since the castings are packed in iron oxide, the carbon on and near the surface is removed and this outer layer adds materially to the strength of the material.

Steel is repeatedly heated during fabrication, and it is necessary to control the rate of cooling very carefully in order to obtain a product of the desired properties. The cooling of iron-carbon alloys of 0.85% carbon or less produces initially coarse crystals. If the material is heated to a point above 690° C., which is the temperature at which all solid solutions break up into the eutectoid of ferrite and cementite, these crystals will disappear and new ones will form. If the heating is not far above the equilibrium line, the crystals will be small. If the temperature is too high, coarse crystals will form again. Obviously only the last heating to which steel is subjected is of importance. The rate of cooling of steel that has been heated to a bright red has a very profound effect on its properties. Very rapid cooling produces a very

hard steel, whereas slow cooling makes a soft steel. There are various theories to account for these effects. One is that some iron remains as gamma ferrite in a state of metastable equilibrium; another assumes that the hardness is due to a solid solution of carbon in iron. It is also contended that hardness produced by rapid cooling is due to great internal stresses. Most metallurgists are inclined to compromise between the allotropic and carbon theories, and consider that both effects are present. If quenching is slower by virtue of using hot oil instead of cold water, the operation is called "tempering," and very slow cooling is known as "annealing." In cooling steels several very definite crystalline forms appear, which are intermediate between the solid solution of carbon in iron called austenite and the eutectic of iron and iron carbide, or pearlite. These forms have definite crystalline forms and physical properties, but represent metastable states in which are present gamma and beta iron and solid solutions of iron carbide in alpha iron. Cooling in such materials as oils or molten and easily fusible alloys is known as tempering; it is also common practice to cool the hardened steel and then reheat to a very definite color and temperature and to follow by quenching in a bath. The temperature to which the metal is reheated governs the hardness. These temperatures of reheating are never very high, 400°C . being about the upper limit for a fairly soft steel.

Case hardening is a process of treating soft steel with carbon so as to produce a very hard and resistant surface layer without losing the toughness and ability to resist strains and shocks of the remainder of the material. The soft steel is heated to around 900°C . in a bath of molten alkali cyanide or in the presence of other carbon compounds, particularly those also containing nitrogen. As the carbon compound decomposes, the carbon penetrates the steel. When the desired amount and degree of penetration is attained, the material is cooled and reheated, and cooled again at a rate necessary to produce the required hardness.

In recent years a considerable number of alloys in which the desired properties are conferred by some other elements than carbon have been developed, and are called "alloy steels" to distinguish them from ordinary or carbon steel. These elements may merely alter the conditions of the iron-carbon equilibrium; they may alter the form in which carbon is present; they may serve to remove oxygen and other gases; or they may form distinct alloys. The more common alloys are nickel steel, manganese steel, chromium steel, silicon steel, and more complex alloys such as nickel-chromium steel and chromium-vanadium steel.

CHAPTER XIX

PETROLEUM

The term "petroleum," derived from two words meaning "rock" and "oil," is a very apt description of this liquid, which occurs in very large amounts beneath the surface of the earth. Petroleum is composed primarily of carbon and hydrogen, with smaller amounts of nitrogen, oxygen, and sulfur. Although petroleum has been known for many centuries, no commercial use was made of it until the middle of the nineteenth century. Attention was directed to the industrial possibilities of petroleum by the development of uses for the by-products of coal carbonization. The distillation of tar yielded a series of oils, the lighter fractions being satisfactory solvents and substitutes for animal and vegetable oils in lamps. Petroleum distillates that had the same physical properties and could be used for the same purposes were known for a long time as "coal oil."

The first petroleum well, known as the Drake well, was dug at Titusville, Pennsylvania, in 1859. Very thorough physical and chemical examinations of the product were made at Yale College by Benjamin Silliman, Jr., who pointed out that decomposition took place at the higher temperatures of distillation with the production of lower boiling liquids. In a few years the petroleum industry began a period of unbelievable growth, both on account of increase in population and industry, and particularly because of the development of new uses for petroleum products. The tide of discovery swept from Pennsylvania westward through West Virginia, Ohio, Indiana, and Illinois. In 1901 the great fields along the Gulf of Mexico began to dominate production. In 1910, California became a great oil state, and in 1913 the Cushing pool in Oklahoma marked the beginning of the petroleum industry in that section of the Mid-Continent region. Some other great fields that have since played an important part in the petroleum industry are the Caddo in Louisiana, Burkburnett, Ranger, Mexia, and East Texas in Texas, and Los Angeles in California. The greatest single factor in the development of the petroleum industry has been

the invention of the internal-combustion engine, and its use in transportation.

Sources of Petroleum. Since the beginning of the petroleum industry nearly three-fourths of all crude petroleum has come from North America, and of this almost two-thirds from the United States, since exploration has been more thorough in the region where there was the greatest demand for the products of the petroleum industry. Over 75% of all passenger cars, buses, and trucks registered in the world are in the United States.

In 1931 the production of petroleum in terms of 42-gallon barrels was in round numbers as follows:

COUNTRY	MILLIONS OF BARRELS	COUNTRY	MILLIONS OF BARRELS
United States	851 4	Poland	4 4
Russia	156 3	Sarawak	3 3
Venezuela	120 1	Japan and Taiwan	2 3
Roumania	46 3	Egypt	1 8
Persia	45 1	Germany	1 8
Mexico	33 0	Ecuador	1 8
Dutch East Indies	32 8	Canada	1 6
Colombia	18 2	Iraq	1 2
Argentina	11 7	France	0 5
Peru	10 1	Others	0 4
Trinidad	9 8		
British India	7 8		
			1361 7

The oil-producing regions of the United States are divided as follows:

Appalachian (New York, Pennsylvania, West Virginia, Eastern Ohio, Kentucky, Tennessee).

Lima-Indiana (Western Ohio and Indiana).

Illinois.

Mid-Continent (Oklahoma, Kansas, Northern Texas, Northern Louisiana, Arkansas).

Gulf Coast (Southern Texas, Southern Louisiana).

California.

Rocky Mountain (Wyoming, Montana, Colorado).

The three states which lead in petroleum production are Texas, California, and Oklahoma, the order in which they stand varying with the opening of new fields and with shifts in economic conditions. The production of petroleum in the United States for 1931 was as follows:

STATES	MILLIONS OF BARRELS OF 42 U. S. GALLONS	STATES	MILLIONS OF BARRELS OF 42 U. S. GALLONS
Texas.....	331.5	Ohio...	5.3
California..	188.8	Illinois.....	5.0
Oklahoma..	181.1	West Virginia..	4.5
Kansas.....	36.9	Michigan.....	3.8
Louisiana..	21.8	New York.....	3.4
New Mexico..	15.2	Montana.....	2.9
Arkansas...	14.8	Colorado...	1.6
Wyoming...	14.8	Indiana.....	0.8
Pennsylvania..	11.8		
Kentucky...	6.4		<hr/> 850.4

In 1929 the three states producing more than 100 million barrels were:

Texas	257.3
Oklahoma	249.9
California	231.8

and in 1930 the figures were:

Texas	290.7
California	228.6
Oklahoma	214.4

Petroleum Resources. Various estimates of the resources of oil in the United States and in the rest of the world have indicated that the present rate of production would leave the United States entirely without oil in a decade, and that in less than a century all the oil in the world would be used up. Such predictions have been made for the past fifty years; the production in the United States has increased markedly over this period, and for a considerable part of the time the industry has suffered from overproduction. Several years ago a committee of the American Petroleum Institute made a thorough survey of the whole situation, having used the vast technical, scientific, and economic resources of the oil industry in the United States in assembling information and drawing conclusions. The conclusions of this committee are quite reassuring, and are briefly these: Existing wells and acreage under production then showed a five-year supply for the world already in sight with the use of ordinary flowing and pumping methods. The use of air, gas, and flooding methods should result in about five times that much more. There are fully a billion acres in this country where the possibilities of finding oil are as good as they were in the territory from which oil has already been taken. This report also states that there is little waste of the oil itself in the course

of its production. Economic authorities, however, generally agree that there is very great waste of natural gas. Since there is no federal or state economic machinery for limiting the number of wells dug in a new field, many more wells are dug than should be, there is great overproduction, and economic conditions are generally badly unbalanced.

Production of Crude Petroleum. Oil fields are characterized by a porous structure constituting a reservoir, an impervious cover, and such geological formations that make segregation of oil and separation of water possible. Petroleum usually occurs in sandstones and sands, although in rare cases it is found in igneous rocks.

It is most generally believed that petroleum is the result of the decomposition by bacterial action, fermentation, or other low-temperature reactions of plant and animal remains. The absence of unsaturated hydrocarbons of low molecular weight indicates that destructive distillation and high-temperature reactions had no part in petroleum formation.

Although some oil fields have been located as the result of accident, the bulk of all exploration for oil is now in the hands of trained and competent geologists, who are able to predict the possibility of oil in a given formation, and who can save a great deal of expense by eliminating fully one-half of the earth's surface as impossible as a location for oil. Geophysical methods of oil finding, or structure discovery, have resulted in very rapid development of oil fields. Such methods include the seismograph, torsion balance, and magnetometer. Paleontology and lithology have had an important part in the exploitation of prospective oil deposits. Obviously the only way oil can be found is to drill for it, but at the same time it is extremely rare that oil is found where scientific study shows that the formations of the earth are not favorable to its collection.

The older method of digging an oil well was by lifting and dropping a heavily weighted cutting tool by means of a cable, the tool being skillfully turned and guided so as to dig a round hole, which is at the same time approximately straight. This method is now being largely superseded by cutting tools suspended by rigid rods, which are positively driven. During the digging process the pipe, known as "casing," is lowered to shut out water and prevent caving of the well walls.

When the oil-bearing strata have been penetrated, very often the pressure of gas drives the oil from the well with such force that its flow cannot be controlled. However, very careful preparations are made for the rapid installation of control valves, and there is much less loss and waste of oil than in former years. Since it is impossible

to store quantities of gas, enormous amounts of this valuable material are lost before pipe-line connections can be made. After a well ceases to flow of its own accord, oil is pumped from it, and when production by this method has practically ceased, additional amounts of petroleum can be obtained by shattering the formation by exploding nitroglycerin. Only a part of the petroleum in a formation is brought to the surface by flowing and pumping. Considerable progress has been made in oil production by methods involving forcing down gas, water, and soda solutions into oil formations. A reservoir that has yielded oil is apt to have below it one or more others, so that wells are being sunk to still lower levels in oil fields. In course of time it is likely that a great deal of oil-bearing sand will be mined and the oil extracted from it.

Composition of Petroleum. In spite of the vast amount of research that has been done on the chemical composition of petroleum, it is still impossible to say with any degree of certainty what compounds are present and in what amounts. The effects of heat during distillation and of the substances used in treating the products of distillation bring about profound chemical changes in many of the compounds originally present. The composition of natural gas is known with a considerable degree of accuracy, and on the basis of this knowledge it is possible to reason by analogy as to the presence or absence of certain types of compounds.

Most oils are made up primarily of hydrocarbons of various types. If sulfur is high, it is entirely possible that the oil may be made up entirely of complex sulfur compounds of large molecular weight in which the number of sulfur atoms is small in comparison with carbon and hydrogen atoms. Such compounds would be prone to decompose to give much simpler sulfur compounds and hydrocarbons free from sulfur. Since the hydrocarbons theoretically possible are almost infinite in number, it has often been said that there is the possibility that any of them may exist in petroleum. In the absence of evidence to the contrary and on the basis also of a great mass of experimental work on the hydrocarbons of petroleum, the conclusion that the number is not extremely large is probably more nearly correct. However, the types of compounds present in crude petroleum may be known with a fair degree of probability, and considerable progress has been made towards positively identifying and separating individual hydrocarbons up to the decanes.

Petroleum from Pennsylvania was once regarded as being made up almost entirely of the saturated hydrocarbons of the C_nH_{2n+2} or paraffin

series. It has been quite definitely proved that the paraffin hydrocarbons in Pennsylvania oil, with the exception of paraffin wax, are limited to the most volatile constituents. Paraffins above $C_{16}H_{34}$ are waxes and not lubricants, and Pennsylvania oils are known to yield considerable amounts of the lubricant fractions. The view is now largely held that crude petroleum contains very considerable amounts of naphthenes, or saturated ring complexes of five to seven carbon atoms in the ring, and polynaphthenes, or polycyclic saturated hydrocarbons.

In natural gas, which accompanies petroleum, no gaseous mono-olefines or acetylenes have ever been found. It is thus reasonable to suppose that no simple olefines are present in the more volatile portions of crude petroleum. Aromatic hydrocarbons are known to be present, particularly the lower members of the series. The sulfur compounds are probably very complex in the original petroleum. By better methods of nitrogen determination, it has been shown that the quantity of nitrogen in crude petroleum is lower than formerly believed. The nitrogen compounds in the kerosene distillates are probably hydro-aromatic in their nature, and have been referred to as "petroleum alkaloids." Compounds of a similar nature have been obtained by heating protein materials in heavy oil. Hence it is likely that the original nitrogen compounds are also quite complex. Some petroleums contain complex acidic substances called naphthenic acids. Recent research indicates that there are several types of these acids, and that for the most part the carboxyl group is at the end of a paraffinic side chain on various types of rings. Resinous materials are probably highly polymerized oxygen compounds. Asphaltic bodies contain varying amounts of sulfur, in some cases up to 5%, and the carbon is probably in polycyclic nuclei.

Physical Properties of Crude Petroleum. Crude petroleum varies in appearance from a pale, straw-colored, transparent liquid up through yellow, red, brown, to almost black shades. Most of it is not transparent and permits the passage of light only through very thin layers. By reflected light most crude oil has a greenish cast, which should not be confused with the blue fluorescence of heavy petroleum distillates.

Various physical tests are made on crude petroleum, both for purposes of evaluation and for making engineering calculations. The specific gravity is usually less than 1.0, although some heavy crudes will run as high as 1.06. The average is between 0.850 and 0.940. The American Petroleum Institute specific gravity scale is commonly used

instead of the Baumé scale. Specific heat is determined for use in refinery calculations. Viscosity has a bearing on the ease with which oil may be pumped through pipe lines and about the plant. Water and such solid matter as sand, rust, and organic sediments are also determined. An ultimate analysis for carbon, hydrogen, oxygen, nitrogen, and sulfur is often made. The information obtained by distilling one or two liters of petroleum in a flask equipped with an efficient column is of considerable value in estimation of possible yields of products in modern large-scale distillation equipment, and also gives an analytical basis of comparison of oils.

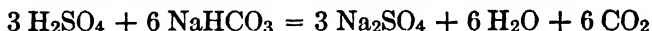
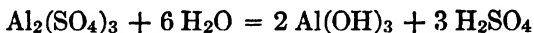
Classification According to Base. An "asphalt base" oil, sometimes called "naphthene base," is one which leaves a thick, asphaltic residuum in the still after all readily volatilizable materials have been removed by fire and steam distillation. No crystals of paraffin separate from the heavier distillates of a true asphalt base petroleum. A "paraffin base" oil, subjected to fire and steam distillation, yields a heavy distillate from which paraffin crystals separate, and the residue in the still is suitable for use as a steam cylinder lubricant. A "mixed base" oil is one that leaves a residue containing some asphaltic material, readily removable to leave lubricating oil stock, and whose distillate yields paraffin crystals.

Transportation Methods. Tank cars are used to a limited extent in conveying crude petroleum from wells to refineries and ports, but the bulk of this material is carried by pipe lines. Some pipe lines extend half way across the continent, as for example from Texas to Illinois, and from Oklahoma and Kansas to the Atlantic seaboard. There are over 90,000 miles of pipe lines in the United States, whose carrying capacity at any one time is said to be nearly 16 million barrels of petroleum. A great deal of oil is handled in tank steamers, particularly that coming from the Pacific and Gulf Coast fields, and from Mexico and South America to the upper Atlantic seaboard. Refineries are distributed largely according to markets and transportation facilities rather than the location of oil fields, both because of the transitory nature of all oil fields, and because it is much cheaper to transport crude oil by pipe line and even by tank car and tank steamer than to ship gasoline and other finished products. Some seaboard refineries supplied both by pipe line and tankers are distributing gasoline by pipe line.

Storage and Fire Protection. Petroleum and its products are commonly stored in low cylindrical tanks of steel, or in some instances in concrete-lined reservoirs. In order to minimize evaporation losses, the

tanks are roofed with steel. Where any number of storage tanks are near each other, as in "tank farms," there are division walls of earth or concrete which separate the tanks. It is necessary to "ground" the tanks to prevent accumulation of electrical charges. The greatest source of danger from fire is from lightning striking a tank. Some of the expedients to cut down loss by evaporation are: tanks coated with aluminum paint to lessen heat adsorption; floating tank covers, which rest on the surface of the liquid and rise and fall as the tank is filled and emptied; water sprays or "water tops" on roofs; "breather bags," and auxiliary equipment that collects the gas expelled with increased temperature and returns it with decreased temperature.

In case of fire, surrounding tanks are kept covered with flowing water, and water is thrown directly in the fire only for the purpose of building up a foam. The method most widely used in controlling and extinguishing an oil fire by means of foam is to flow on to it a froth made by the action of a sodium bicarbonate solution on another solution of aluminum sulfate. The reactions that take place involve the hydrolysis of the aluminum sulfate, which is very slight in water solution but very rapid when the acid formed is used up by sodium bicarbonate.



The bicarbonate solution also contains an organic compound of some sort, which serves to make the precipitated aluminum hydroxide colloidal. The bubbles of carbon dioxide become covered with a coating of the hydroxide, so that a thick blanket of froth covers the burning oil and not only insulates it but shuts off the air and tends to prevent the escape of oil vapors. The liquids are commonly handled in separate pipe lines and mixed at a common nozzle, but another method is to add a dry mixture of the sodium bicarbonate, aluminum sulfate, and organic peptizing agent to water, and pump the froth to the point where it is needed. The froth does no harm to equipment, ultimately dries out, and can be brushed off. Some progress has been made in protecting tank steamers and storage tanks by means of cooled and scrubbed flue gases.

THE REFINING OF PETROLEUM

Refining petroleum includes the separation by distillation of the crude petroleum into a series of fractions, the thermal decomposition

of certain of these fractions to form more volatile products, and the further processing of all products to meet specifications. The application of modern chemical engineering methods has resulted in sweeping changes in the refining operations, and most processes are continuous.

Distillation operations may be roughly divided into two types, topping and complete. The second type is of three kinds, depending on the residue left in the still: to cylinder stock, to flux, and to coke. The "topping" or "skimming" operation involves a partial distillation with the removal of only the more volatile material. The product of such distillation may be gasoline, or gasoline and kerosene; the residue is commonly used as a fuel oil. Until recent years the topping operation was entirely separate from subsequent thermal decomposition or "cracking" of the gas oil fraction. Some modern plants are combining crude topping, the cracking of both crude and gas oil, stabilization of the gasoline, and in some cases "reforming" the naphtha to a high anti-knock gasoline. The products of these combination units are straight-run gasoline, stabilized cracked gasoline, and specification fuel oil. Such units conserve refinery fuel and result in a number of economies as well as a lowering of investment costs, and indications are that they will be increasingly used in the petroleum industry.

If distillation is to be carried to cylinder stock, the crude must be of the paraffin or mixed base type, so that the residue may be worked up into lubricating oils. Running to flux is the method commonly used where the residue will not make a satisfactory lubricant, even if distillation is stopped at the same point as with the previous method. Lubricants are not made by this operation, but only from distillates. The residue is a thick, asphaltic material, and is either used while still hot as fuel in the refinery, or more commonly as a road or roofing asphalt. Running to coke represents a method that is practiced much less now than formerly in the distillation of crudes. As the term implies, it involved the continuation of heating until all material that could possibly be converted to a vapor had been removed, and what remained in the still was a porous substance composed mainly of carbon. Such distillation is accompanied by a great deal of thermal decomposition or "pyrolysis." Some lubricating distillates are rerun to coke in order to bring about changes in some of the compounds that in the original distillate prevented the proper crystallization of the paraffin wax.

The types of stills used in the petroleum industry represent a most interesting evolution as chemical engineering increased its influence on

this industry. The earliest form of distillation equipment is the *shell still*, which is essentially a steel cylinder with curved ends whose length is approximately three times its diameter, and which is set horizontally in brick over a firebox, and heated on its lower surface by a direct fire. The ends and upper half are covered with a thick layer of insulating material. A typical 1200-barrel shell still is 45 ft. long and 15 ft. in diameter. This type is still extensively used, but is by no means as important as in the earlier years of the industry. In order to increase heating surface and to insure circulation, a shell still may be equipped with a series of flues to carry hot gases. The supply of heat may be further supplemented by the use of steam, which is admitted through perforated pipes below the surface of the oil. There is not only the stirring, which is very desirable, but also the "steam distillation" effect. Steam distillation is quite commonly carried out under greatly reduced pressure, the stills being equipped with vacuum pumps. If liquids are condensed and only fixed gases pass through the pump, the operation is called "dry." "Wet vacuum" means pumping liquids and gases together. In order to secure close temperature control in the distillation of high-grade lubricants, a few refineries use no direct heat from a fire, but transfer heat by means of very high-boiling substances such as diphenyl and mercury.

"Flash distillation," or the heating of very small quantities of a liquid at a time to a sufficiently high temperature to convert all the volatile substances desired as products into vapor with fractional condensation, has some important advantages over the older system of progressive heating of a large mass of liquid with the continuous removal of vapors as a series of cuts of decreasing volatility. Flash distillation very greatly lessens decomposition because of the short time involved, and it always produces the same products rather than materials of constantly changing viscosity and specific heat. Thus the heat exchange equipment can be much better designed than for a "batch still," where light products are removed in the first part of the distillation and heavy products in the later stages. Flash distillation permits the use of lower temperatures through taking advantage of the mean boiling point of the fraction vaporized. In order to employ this principle as much as possible the petroleum industry is increasingly using the *pipe still*. This is essentially a series of coils of pipe set in a heating chamber, the oil being fed at high velocity through these coils and discharged to fractionating columns. The high velocity facilitates heat transfer, since the oil is in the favorable condition of "turbulent flow" with consequent lower film effects, and also does away

very largely with deposits of coke and salts. The oil fed to such stills has already passed through heat exchangers. Pipe stills may be operated at reduced pressures, at atmospheric pressure, and when heavily constructed, at very high pressures.

The earlier refineries made no provision for heat exchange. Distillation was a batch operation; the crude was fed cold; and vapors were condensed with considerable refluxing. Improvements included substitution of continuous for batch distillation; eliminating coking stills as far as possible; and preheating the feed by means of escaping vapors and the hot residues from preceding stills. Modern methods of heat exchange have cut down fuel costs in a refinery to a fraction of their former value, and the greater efficiency of pipe stills has added still more to the utilization of fuel.

The first steps in the direction of fractionation involved exposed vapor lines, heat exchangers serving as partial condensers, air-cooled towers in series, and perforated plate towers. Packed towers have had extensive use, but the modern petroleum refinery has finally gone over to the more efficient bubbling cap column or tower for fractionation. The towers may be equipped with reboiling coils at the bottom, and often a portion of the tower known as the "stripping section" has facilities for the injection of steam.

A portion of the condensation of vapors is accomplished in heat exchangers. In a vapor-liquid heat exchanger the liquid is in the tubes surrounded by the vapor. Final condensation is accomplished by the use of water as a cooling medium. A very common type of condenser is the "submerged coil." The "shell and tube" condenser is much the same as a vapor-liquid exchanger, the cooling water usually being in tubes and the vapors outside them in the shell. Barometric jet condensers are used to some extent. Heat exchangers not only function as condensers, but are also extensively employed to transfer heat from residual hot oil from stills and columns to cold material that is fed to a still. They may be of the shell and tube type, or merely double pipes with the feed flowing through the inner pipe and the hot residual oil through the annular space around it in the outer pipe and in an opposite direction.

The assembly of heat exchangers, stills, towers, and condensers into a complete installation is capable of infinite variations. The products and the raw material are important factors in determining the way in which refineries are designed and operated. The two main considerations in all petroleum distillations are time and temperature. In order to avoid cracking, everything possible is done to reduce the time during

which the oil is subjected to heat and to minimize the temperature of distillation. If a crude is to be refined for either asphalt or residual lubricating oil, it is essential that cracking be prevented as far as possible. If only shell stills are available, excessive quantities of steam are used, not only for steam distillation effects but also for preventing the oil adjacent to the still bottom from becoming overheated. Wet vacuum is still better than the use of steam alone. Best of all is the most modern equipment, vacuum pipe stills, in which both the temperature and time of heating are reduced to the minimum. On the

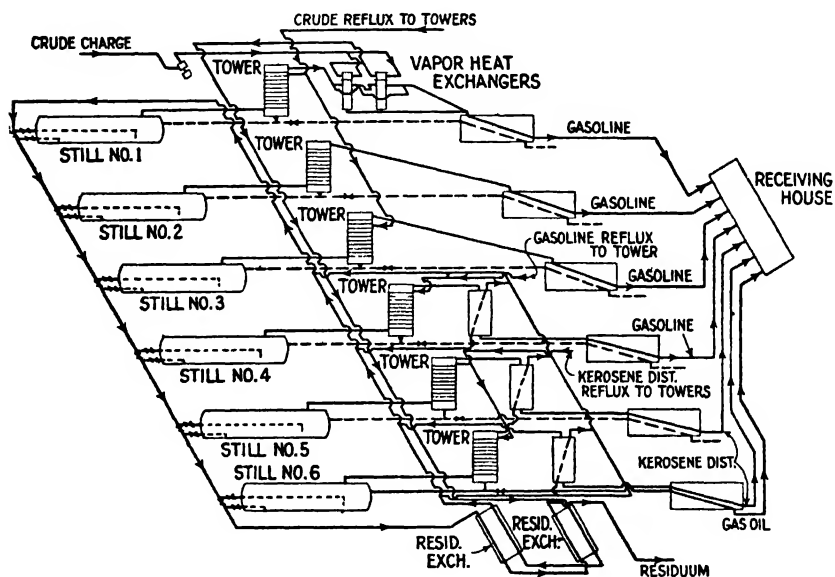


FIG. 93.—Continuous Distillation with Shell Stills. Courtesy The Texas Company, New York City.

other hand, if a crude is to be run only for fuel oil, gasoline, and cracking stock, there is very little advantage in the use of vacuum distillation equipment.

In "American Petroleum Refining" (Second Edition), Bell cites a number of examples of the methods employed in refineries to meet different distillation requirements. These involve shell stills, pipe stills, and combinations of the two types, bubble towers, heat exchangers, reboilers, flash towers, flash drums, preheaters, fractional condensers, final condensers, and coolers. There are so many different requirements and ways of meeting these requirements that citing all of them would be bewildering, and citing only one or two would be

misleading. In general, it may be said that the oil is heated in the most efficient and economical way possible; as much heat as possible is conserved; and fractionation is done to the extent required by the nature of the products to be made. Ordinarily a single still delivers a single product from its column and condensers, but it is possible to operate a single pipe still with a column equipped with a reboiler so that gasoline, "water white distillate" (from which lamp oils and high-grade furnace oils are obtained), gas oil, and fuel oil residue can be

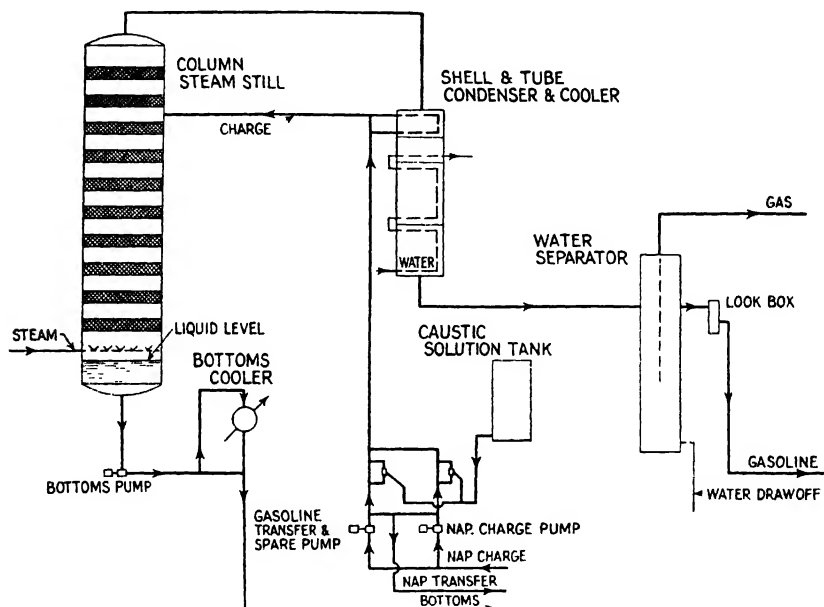


FIG. 95.—Distillation of Naphtha with Column Steam Still Courtesy The Texas Company, New York City.

made, there being no recirculation of oil through the still. Most distillations involve a series of stills, those producing the more volatile materials being equipped with columns.

Topping may be accomplished by the use of pipe stills. They may also be used as "viscosity breakers" in which residual oils give a certain amount of gasoline and gas oil in addition to a low-viscosity fuel oil.

Cracking Processes. The term "cracking" in the petroleum industry refers to pyrolysis, or thermal decomposition, of carbon compounds. The whole object of cracking is to break up hydrocarbons of higher boiling point and greater molecular weight into more volatile and

lower molecular weight products suitable for use in internal-combustion engines. The higher the molecular weight, the easier it is to decompose a hydrocarbon by heat. In general, the effect of heat at ordinary pressures is to produce lighter from heavier hydrocarbons with little gas formation up to around 500°C . Above this point, gas is formed increasingly. At 700°C ., gas oil sprayed on checker brick decomposes largely into hydrocarbon gases, both aliphatic and aromatic liquid hydrocarbons of low molecular weight being made. By the time 900°C . is reached, aromatic hydrocarbons are the primary liquid products. From 1000°C . up, methane, hydrogen, and carbon are the products of pyrolysis. Pressure serves to oppose the formation of gas. The longer the time of heating, the more complete are the pyrolysis reactions.

Cracking is therefore increased by raising the temperature of the hydrocarbons used and by lengthening the time of heating. The various industrial cracking processes differ from each other primarily in the way in which they accomplish these two purposes and at the same time meet the chemical engineering requirements of preventing coke deposition, securing high heat transfer, and working within the safe limits of available equipment. The development of modern chromium-iron and nickel-chromium-iron alloys has made possible the use of very high pressures at temperatures far beyond the limits of safety of ordinary steel. If it is desired to use extremely high temperatures, safe operation will not permit high pressures, and therefore the "vapor phase" processes operating at relatively low pressures are employed. On the other hand, if lower temperatures are used, high pressures not only can be afforded but actually are needed in order to give the necessary time element. Where high temperatures are used, very high velocities are required in order to keep the heating surface clean, and again it becomes desirable to maintain low pressures. Low pressure-high temperature operations are always characterized by excessive gas production. As the pressure is raised, this gas production is reduced, but simultaneously fuel oil production is increased because of polymerization. As a result of this polymerization, however, the gasoline is a more stable product although perhaps slightly poorer in anti-knock quality.

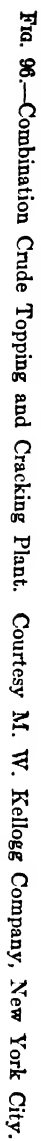
The choice of material to be subjected to cracking processes is primarily economic. Materials in the kerosene range have ready sale at a price that does not make their use as cracking stock profitable. Although there is an increasing demand for still higher boiling products as furnace oils, the price realized for such products for this pur-

pose, and also as gas oils for enriching water gas, is not sufficient to interfere with their profitable use as cracking stock for making motor fuel. While still higher boiling oils are even more easily cracked, they have great value as lubricants, and in their production are protected by the use of steam and vacuum. Considerable quantities of heavy residual oil are now being cracked and some work is being done on the cracking of crude petroleum, but the bulk of cracking stock is material in the gas oil range. On the other hand, a great deal of straight-run gasoline is being "reformed" by heating it in pipe coils to pressures of the order of 2000 lb.

The utilization of cracking processes has greatly increased in recent years. The demand for motor fuels could never have been met economically on the present production of crude petroleum if it had not been for the wholesale cracking of gas oil. Yields have increased with higher temperatures and pressures, and the residual material from such operations still finds a market as a fuel. There have been thousands of patents on a very great variety of processes, but only a few are in general use and need to be described as typical. Cracking processes may be classified in two divisions, liquid phase and vapor phase. When there arose a demand for aromatic hydrocarbons for explosives, vapor phase processes were developed, but with the return of normal conditions they were largely abandoned. Recently vapor phase cracking has become important because of the "anti-knock" properties of its products.

The equipment used in cracking processes includes heated tubular elements, chambers in which pyrolytic changes continue, separating and fractionating apparatus, coolers, heat exchangers, and pumps. Hence flow sheets of cracking plants will have many things in common, although the actual processes will be quite different in method and effect.

As noted before, in some of the most modern refineries the cracking process is very closely interrelated with the preliminary operations to which the crude oil is subjected. This principle is illustrated by a plant in which the cold crude is preheated by vapors from an evaporator tower, and is fed to a "crude flash tower" for the purpose of obtaining from it a light, straight-run gasoline and heavy naphtha. The hot topped crude is run through a "black oil furnace" in the tubes of which it undergoes mild pyrolysis with the result that there are large yields of gas oil, which are cracked either in liquid or vapor phase, and a correspondingly smaller amount of residual fuel oil. This is combined with the residues from the gas oil cracking operation.



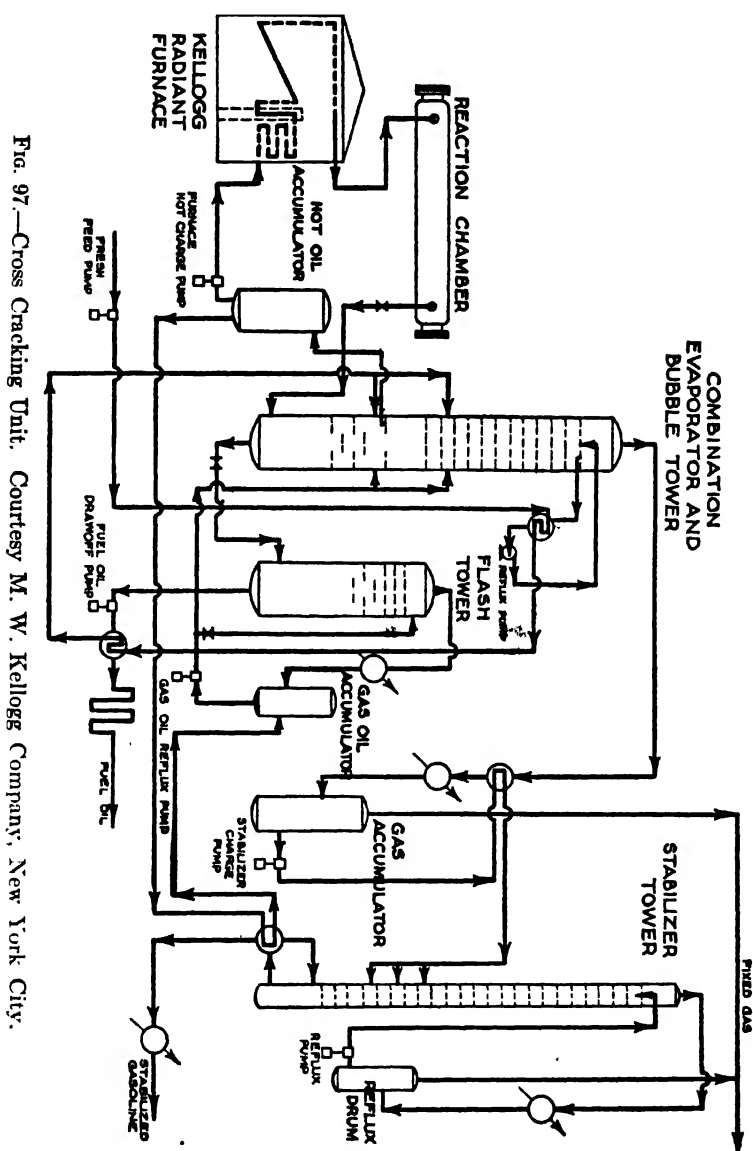
LIQUID PHASE PROCESSES. The earliest successful cracking process, and one by which many millions of gallons of gasoline have been made, was the Burton process. In this process the gas oil was heated in a series of inclined tubes terminating in headers and connected with a horizontal shell protected from direct heat. The operating pressure was about 95 lb. per square inch. When the accumulation of a carbonaceous solid residue made the heat transfer surface ineffectual, the still was shut down for cleaning.

The principle of most modern liquid phase processes is to heat continuous streams of oil under high pressure in cracking coils, deliver the heated oil to unheated but insulated reaction chambers, and from these to draw vapors to fractionating towers and to separate the residue as a fuel oil. The towers serve to separate the gasoline and naphtha and fixed gases from intermediate fractions which may be advantageously recycled. The details of processes vary considerably, and a few will be discussed as typical.

Cross Process. Gas oil is preheated by reflux and in some cases by hot fuel oil and is fed into the lower part of a fractionating bubble tower, where it mingles with the heavier fractions returned by the upper plates and is fed to a hot oil accumulator. In some cases the hot gas oil is fed to the upper part of the evaporator section of the tower system, where it undergoes partial distillation. The oil is then heated to approximately 925° F. at a pressure of 750 lb. in a tubular furnace and passes to a horizontal reaction chamber, where it remains under this pressure to allow more time for the pyrolytic reactions. Here a "synthetic crude" is formed and is fed with reduction of pressure to 150 to 250 lb. to the bottom of the combination tower. The vapors from the top of this tower are condensed in heat exchangers and are freed of fixed gases in a stabilizer tower. The "bottoms" of the combination tower go to a flash tower in which gas oil is produced as a distillate and fuel oil as a residue.

Dubbs Process. A combination of tube furnace, vertical reaction chamber, dephlegmator tower, flash chamber, and flash dephlegmator characterizes this process. Other features include feeding raw oil to the flash dephlegmator to carry down the column material which is too heavy; withdrawal of the hot residue from the reaction chamber to the flash chamber, where pressure is reduced, and additional vapors are formed which go to the flash dephlegmator, those which are not removed by the scrubbing of the raw oil condensed as "flash distillate"; supplying the main dephlegmator with the bottoms of the flash dephlegmator at a point considerably above where the vapors from the

reaction chamber enter; the recycling of the bottoms of the dephlegmator through the furnace; the condensation of the vapors from the



top of the dephlegmator under pressure; and a return of a part of this condensate as reflux to the column from which it came. The residuum

is drawn from the bottom of the flash chamber and used as a fuel oil. The pressure in this process is of the order of 200 lb.

Tube and Tank Process. The raw oil is fed through the top of the bubble tower and thence through the cracking coil. The heated oil at 850° F. and at pressures of the order of 750 to 1000 lb. is run into the bottom of the reaction chamber or "soaking drum." Liquid overflows into the lower part of the bubble tower, which functions as a separating chamber, the pressure being dropped to 60 lb. Tar is taken from the bottom of the tower, recycle oil from the middle of the tower, and

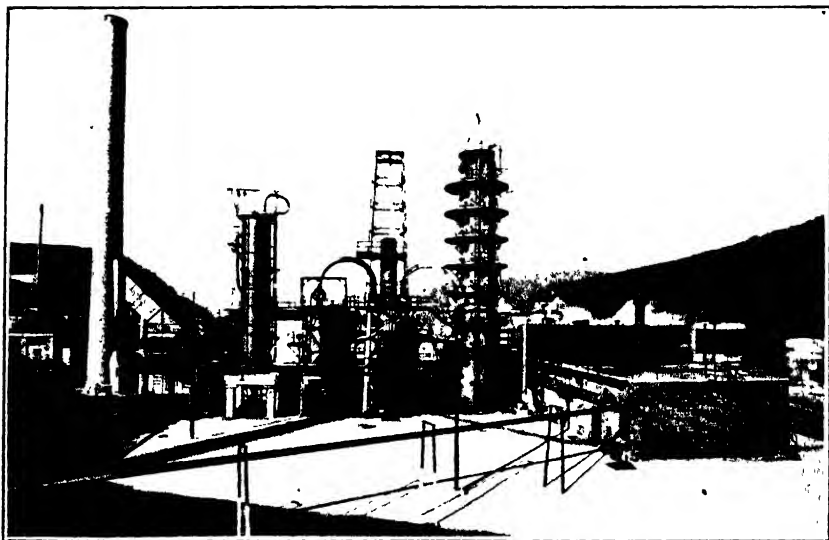


FIG. 98.—Dubbs Process Plant. Courtesy Universal Oil Products Company, Chicago, Ill.

vapor from the top of the tower. The coils carrying the raw oil serve as a partial condenser to provide reflux. Condensation is carried out under pressure, gases being removed from the top of a pressure receiver, and the distillate for the production of gasoline being taken from its bottom. Cold raw oil may also be fed into the bottom of the reaction chamber.

Holmes-Manley Process. This is a process which operates at intermediate pressures of 300 to 400 lb. and at moderate temperatures, chief reliance being placed on time of "soaking," that is, the time the heated oil remains in the reaction chambers. Fresh feed is passed through the coils of a reflux condenser serving as a heat exchanger, is mixed with

recycle stock by being admitted either in whole or in part to the lower part of the bubble tower, and is passed through a tube furnace. The highly heated oil passes to a series of four connected reaction cham-

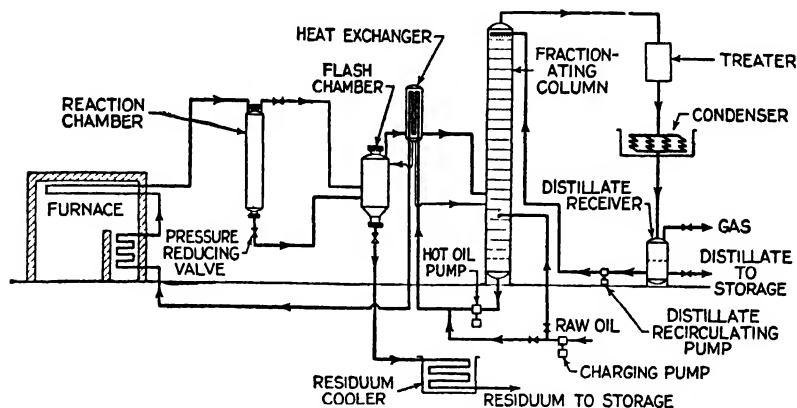


FIG. 99.—Dubbs Cracking Unit. Courtesy Universal Oil Products Company, Chicago, Ill.

bers, which are only partly filled and which are referred to as “vertical stills.” Present practice is to carry lower liquid levels in these stills than in the earlier years of this process. The vapors from the last of

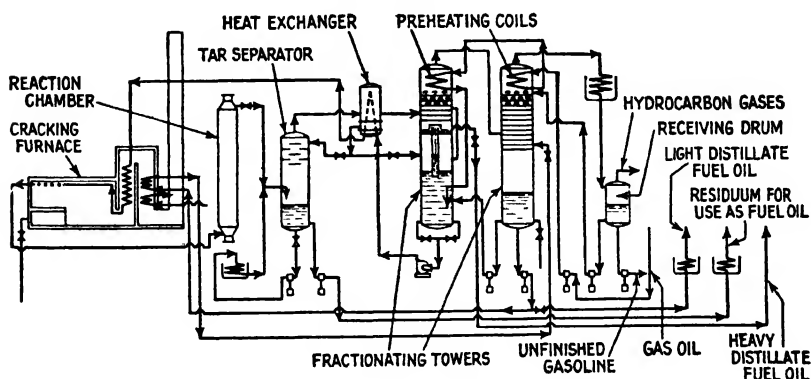


FIG. 100.—Tube and Tank Cracking Unit. Courtesy Standard Oil Company of New Jersey, Technical Service Division. Elizabeth, N. J.

intercommunicating stills pass into a bubble tower equipped with a reflux condenser-heat exchanger. The bottoms from this column are recycled and the vapors are condensed under the same pressure as the

remainder of the system. The condensate passes to accumulators at 80 lb. pressure, from which fixed gases are removed. The bottoms of the four stills pass to a "tar stripper" tower, which operates at atmospheric pressure, from which is obtained naphtha, recycle gas oil, and a fuel oil residue. The naphtha is condensed in the same way as the main product, and part of it is returned from an accumulator to the tower.

The yields from these liquid phase processes vary with the time of heating and with the amount of recycling. The "once through" process gives from 28% to 45% on the basis of gas oil used, and recycling may give as much as 65%.

VAPOR PHASE PROCESSES. A temperature of 950° F. is regarded as the upper limit of liquid phase operation. Since at temperatures somewhat lower than this only excessive pressures will prevent formation of large quantities of vapor, some vapor phase cracking accompanies liquid phase operations in most cases. Vapor phase cracking is ordinarily from 1000° F. to 1200° F. and is carried out at pressures considerably lower than those for liquid phase cracking. Relatively volatile materials can be cracked that could not be handled in the liquid phase. The cost of heating vapors is higher in proportion to their weight. More gas results from vapor phase cracking. As pointed out earlier, this type of cracking has justified its use by producing gasolines of high anti-knock value. Following are two typical vapor phase processes.

Gyro Process. The feed is sprayed against the cracked vapors to bring about partial condensation, at the same time losing its more volatile components, is heated, and passes to a hot oil reservoir, which is below a fractionating column. Any excess beyond that needed is passed through heat exchangers and returns as cold oil, while the remainder is sent through coils and further heated by waste gases from the main cracking furnace. In these coils a mixture of liquid and vapor is produced, which is sent to an evaporator. The liquid is removed as fuel oil while the vapors are mixed with a small amount of steam and sent to highly heated tubes equipped with concrete cores impregnated with iron oxide as a surface catalyst. The vapors, after being sprayed with crude oil, pass into a fractionating tower. The bottoms from this tower are recycled and the vapors are condensed, cleared of fixed gases, and become stock from which gasoline is made.

DeFlorez Process. A distinctive feature of the deFlorez Process is that no oil is fed to the cracking furnace until it has been distilled as well as subjected to a preliminary cracking operation. The process

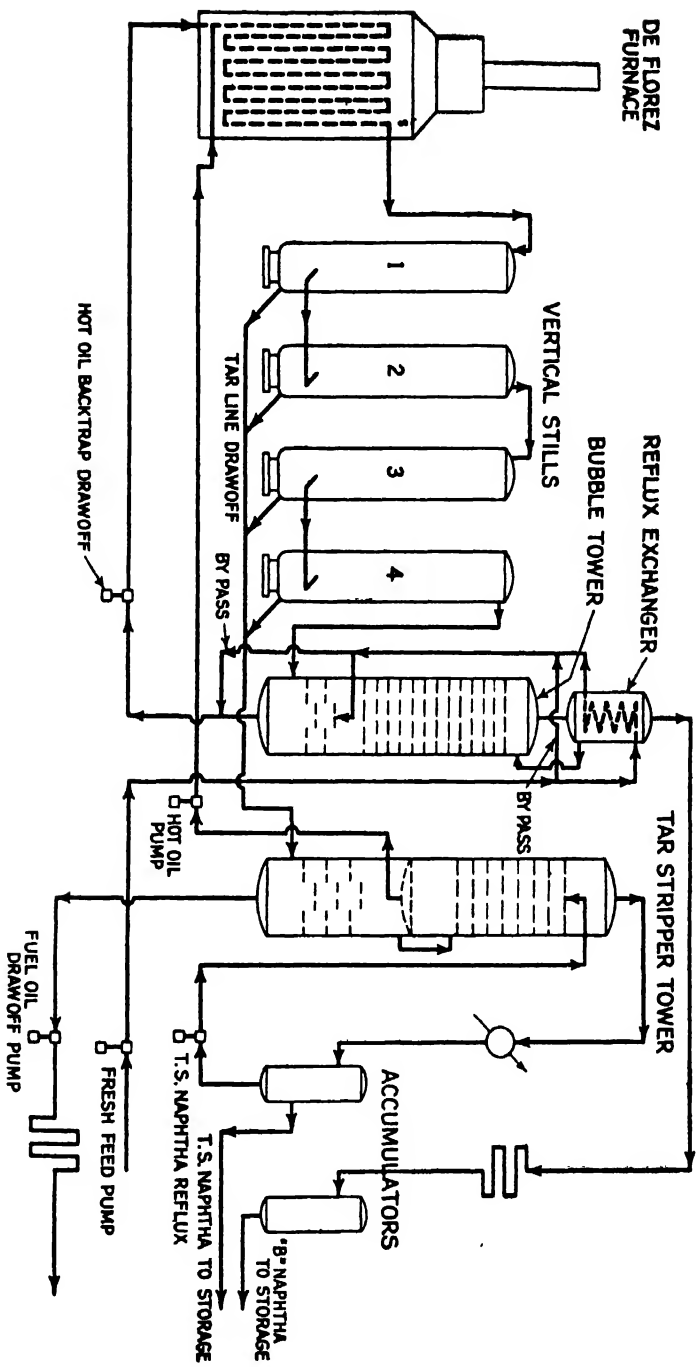


FIG. 101.—Holmes-Manley Cracking Unit. Courtesy M. W. Kellogg Company, New York City.

operates at a pressure of 175 lb., which obtains both in the furnace and in the product separating equipment. The oil may be heated to a temperature as high as 1050° F. in the furnace. The preheated feed is introduced into an evaporator tower where it meets vapors from the furnace. Both distillation and cracking result. Vapors from this tower go to a bubble tower where separation takes place into a raw gasoline which must be stabilized and a gas oil. A portion of the latter taken from near the bottom of the bubble tower is used to preheat and reboil the gasoline for the stabilizing unit and then is fed into the top of the evaporator tower. The remainder drawn from the bottom of the bubble tower is fed directly to the cracking furnace. The bottoms from the evaporator tower are fractionated in a flash tower at pressures ranging from atmospheric to 50 lb., separation being made into fuel oil bottoms, a heavy distillate, which is returned to the middle of the evaporator tower, and a light distillate, which is condensed and fed to the bubble tower for accumulation with furnace charging stock.

The deFlorez furnace is a vertical cylindrical shell lined with vertical tubes set in a circle and with the heat radiating gases passing upward through the center of the furnace and over a series of horizontal tubes which function as an economizer and preheater.

Aluminum Chloride (McAfee) Process. Gas oil is heated with anhydrous aluminum chloride as a catalyst with the production at the same time of light fractions, and a coke residuc. The gas oil is charged into a vertical "cheese box" type still equipped with stirrers together with 10 to 25 lb. anhydrous aluminum chloride per barrel of oil. Temperatures of around 550° F. are maintained. Drums functioning as reflux condensers prevent the escape of the catalyst and permit the removal of vapors at 350° F. The residuc is drained from the coke and aluminum chloride; the vapors are gasoline stock and require no chemical treatment other than alkali wash to remove any traces of hydrochloric acid or catalyst. Vapors from a pressure cracking still may be introduced into the still containing boiling oil and aluminum chloride with the production of a saturated gasoline.

Hydrogenation. Hydrogenation is not yet a process which is in such general use that it has materially affected the industry, either from the standpoint of quality of products or of cost of production. On the other hand, it has passed from the stage of small-scale to large-scale operation, but is still in the experimental stage. The results so far have been most encouraging, and it is freely predicted that hydrogenation will revolutionize the whole industry.

The general method involves mixing the oil with highly compressed

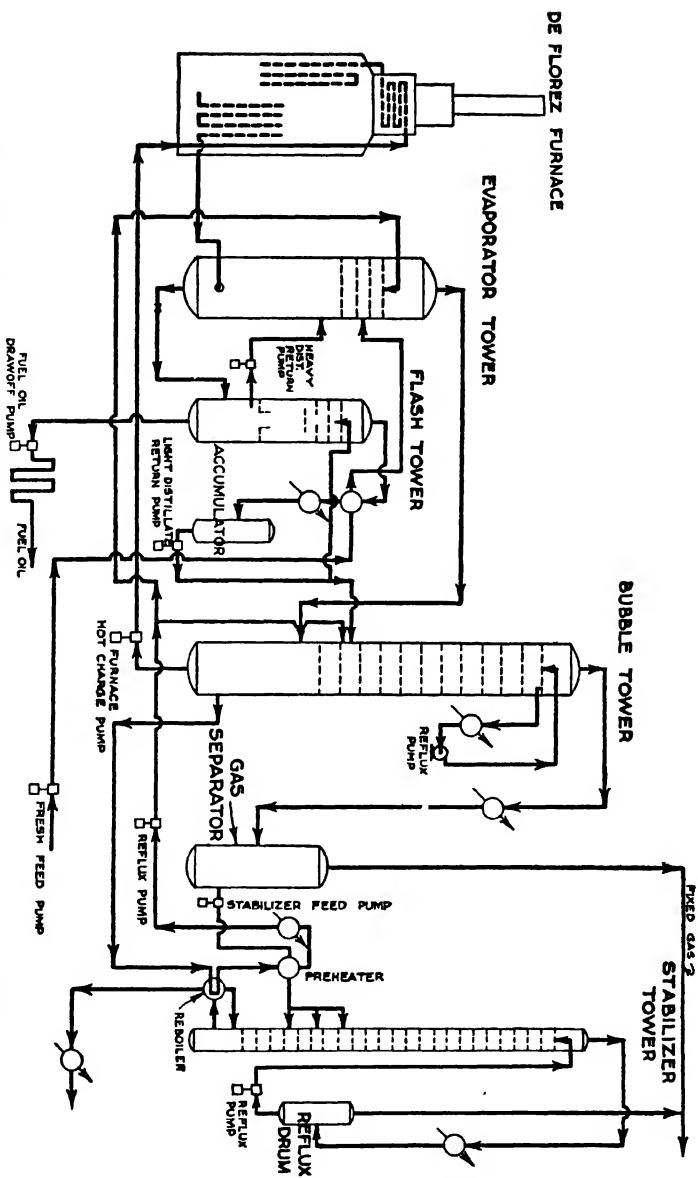
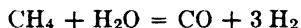


Fig. 102.—DeFlorez Cracking Unit. Courtesy M. W. Kellogg Company, New York City.

hydrogen and forcing the mixture under pressures of the order of 3000 lb. through heat exchangers and direct-fired pipe coils into a vertical cylinder containing a catalyst that is insensitive to sulfur compounds. The reactions are exothermic, and the temperature rises to 1000° F. The products are withdrawn, partially cooled in heat exchangers, and after further cooling are sent to high-pressure separators. The liquid is drawn off, and the gases, still under high pressure, are sent to oil scrubbers. Hydrogen sulfide from the sulfur compounds of the oil is the main impurity of the hydrogen, and is removed by solution in the oil. The hydrogen passes through "booster" compressors, make-up hydrogen is added, and the process is repeated. Practically no coke is formed, and the catalyst is effective for long periods, runs of eight months having been recorded. The hydrogen does not have to be very pure, and can be made either by the water gas process described in Chapter XII or waste refinery gases and natural gas may be used as a source of hydrogen, the principal component of both these gases being methane. Methane, for example, reacts with steam thus:



The carbon monoxide is converted to carbon dioxide with steam with the production of additional hydrogen. Carbon dioxide is easily scrubbed out.

The process is extremely flexible and may be used in a number of ways, which include improvement both of raw materials and final products. The whole nature of crude petroleum and refinery residues is changed, becoming more paraffinic with removal of asphalt and lowering of sulfur content to a fraction of the former value. Poor, off-color, and heavy furnace oils or light gas oils are changed to a material that will yield good gasoline and burning oils. Highly colored, cracked, gum-forming naphthas, high in sulfur, are improved in color and freed of gum and sulfur without change in distillation range and with an actual slight gain in anti-knock properties. Low-grade lubricants are greatly improved by hydrogenation so that they meet varied requirements of high flash, low carbon residue, and a flat temperature viscosity relationship.

Paraffinic gas oils are converted into anti-knock gasoline. The process of hydrogenation represents an equilibrium and is usually controlled by high pressure and great excess of hydrogen. In making anti-knock gasoline, hydrogenating conditions characterize the start of the process, but gradually conditions are shifted until there is slight

dehydrogenation. Excessive dehydrogenation and formation of undesirable gum-forming compounds are prevented by the presence of hydrogen under pressure. A high-flash safety gasoline, which also has high anti-knock rating, has been developed for use in aircraft. High-flash gasolines made by ordinary distillation or cracking have low anti-knock value, which cannot be sufficiently raised by tetraethyl lead. Hydrogenation is also responsible for some very valuable special solvents.

Yields are often over 100% by volume, but where anti-knock properties are to be developed from products already saturated, yields are sacrificed, and may not be over 85%. The statement has been made that widely different results may be obtained from the same crude, hydrogenation giving products ranging all the way from paraffins to aromatics according to operating conditions.

The process of hydrogenation of petroleum and its products is an outgrowth of the Bergius process for the hydrogenation of lignite and lignite tar in Germany, a country that is practically without petroleum resources. Powdered coal is suspended in a heavy tar to form a paste, which is heated in exchangers and mixed with hydrogen under heavy pressure in long reaction cylinders set vertically in concrete stalls. The products are handled after the fashion of petroleum. Something like 36,000,000 gallons of motor fuel were made from lignite tar in Germany by this process in 1929.

PRODUCTS OF PETROLEUM REFINING

Some of the materials which result from the processes described above are ready for market, but others must be further processed. In general, it may be said that the products of initial distillation are gases, gasoline, solvent naphtha, lamp oils, furnace oils, gas oils, lubricant and wax distillates, and residues, which vary all the way from steam cylinder stock through fuel oil and asphalts to coke.

Gasoline. This term may be broadly applied to all the more volatile liquids derived from petroleum. Some of these liquids, whose uses depend on their varying degrees of volatility, are called "naphthas." The bulk of these materials, however, are used as motor fuels, and are generally known as gasoline. In this connection it should be noted that the term "benzine" refers to "cleaners' naphtha" or "Stoddard Solvent" and means a mixture of hydrocarbons somewhat less volatile than gasoline and not the simple aromatic hydrocarbon, C_6H_6 , benzene or benzol. The term is an unfortunate one and should be discarded.

The volatile substances that may be classified together as gasoline result, as previously shown, from two processes: straight distillation of crude petroleum, and thermal decomposition of heavier hydrocarbons either in liquid or vapor phase. Whatever their sources may be, these materials have passed through bubble towers and have been fairly cleanly separated both from gases and extremely volatile liquids on the one hand and from the heavier and less volatile substances on the other. Where bubble towers are used in atmospheric distillation of crude petroleum, the fixed gas contains a small quantity of heavier hydrocarbons, which are recovered and added to gasoline. When the bubble tower is operated under pressure, as is the case in some cracking processes, the gases may contain certain amounts of hydrocarbons, which can be recovered by scrubbing with gas oil and distilling the enriched oil and are returned to gasoline. On the other hand, the gasoline itself, after condensation under pressure, contains fixed gases such as propane and lighter hydrocarbons, which must be removed before the gasoline is marketable. Gasoline containing very volatile hydrocarbons is apt to cause "gas lock," which is a stoppage of gasoline flow in carburetor and feed lines due to a gas seal. Cracking coil distillates are stripped of their gas and more volatile fractions—a process known as "stabilization"—and these are fractionated under heavy pressure. These lighter products find use as fuels in the refinery, as a source of a number of alcohols and esters, for enriching gases in manufactured gas, and as domestic heating and lighting gas, being shipped and handled in pressure cylinders.

The statement is made that in 1930 the gasoline recovered from refinery gases amounted to 11% of the total gasoline production of the United States. This is indeed a tribute to the technical progress of the industry along the lines of conservation.

Some straight-run gasolines are doubtless made up of completely saturated hydrocarbons, both straight chain and naphthenes. Others have some olefines from thermal decomposition, and still others contain aromatic hydrocarbons, which were present, either as such or in more complex form, in the original petroleum. The products of cracking processes contain very considerable amounts of unsaturated hydrocarbons, and those from vapor phase cracking have some aromatic hydrocarbons even when there were no aromatics in the original oil. The sulfur compounds of the original crude are probably well broken up, and the gasoline contains mainly hydrogen sulfide, mercaptans, sulfides, disulfides, thiophenes, and some oxidation products. Certain unsaturated hydrocarbons, probably diolefines, are regarded as

the cause of subsequent gum formation through intermediate oxidation products and their polymerization. By proper refining it is possible to remove gum-forming compounds and at the same time leave in the gasoline large percentages of stable olefines. Color is probably due to highly colored unsaturated hydrocarbons, their oxidation products, and the oxidation of sulfur compounds.

Ordinarily the first step in the chemical treatment of gasoline distillates is washing with concentrated sulfuric acid. The acid is generally of the concentration known as "66°" or about 93%, but some 98% acid is used. The amount required varies with the quantity of sulfur present since only very little acid is required to stabilize cracked gasoline. Some gasolines require no acid at all, whereas high-sulfur gasolines may use as much as 8 lb. per barrel. Not all the unsaturated hydrocarbons are removed, and only the more reactive and unstable ones undergo changes. There is practically no sulfonation. Some acid esters are probably formed by the addition of HSO_4^- and H^+ to double bonds, and these hydrolyze to alcohols. Some sulfur compounds are likely oxidized and dissolved. Some olefines are polymerized, and there may be condensation of olefines with aromatics. Colloidal suspensions of tars resulting from polymerization are precipitated. A part of the products dissolve in the sulfuric acid, but others go into the gasoline layer. In some cases the products of acid treatment are much higher boiling than the substances originally present, and the gasoline thus requires redistillation.

Vapor phase adsorption of undesirable substances by means of fullers' earth in towers has somewhat limited application. Some progress has been made in sulfuric acid treatment at very low temperatures, and also in the use of magnesium hydroxide and zinc chloride.

Sulfuric acid is mainly removed by washing with water, but the last traces of acid are taken out by a solution of caustic soda. Gasoline containing appreciable amounts of sulfur compounds is treated with sodium plumbite solutions. These solutions are the result of the action of caustic soda on litharge, PbO , and are known as "doctor" solutions. Their effect is not to remove the sulfur completely, in fact since powdered sulfur is often added during the treatment, more sulfur may be present afterwards than before. Hydrogen sulfide is certainly removed, and mercaptans are converted into disulfides, which are harmless and which remain in the gasoline. Sodium hypochlorite is used to some extent in the treatment of gasoline. The effect seems to be oxidation of some of the sulfur to sulfate and the conversion of other compounds to disulfides. It is thus evident that not only total

sulfur compounds but also the nature of the sulfur compounds present are important considerations. In warmer weather it is doubtful whether the burning of the sulfur of gasoline does any harm. In winter the condensation of steam from the exhaust and the solution of sulfur dioxide cause some corrosion, but the effect is slight.

In order to avoid evaporation losses that characterize air agitation in batch methods of treatment, modern refineries carry out chemical treatment of gasoline continuously in a series of towers. In one system the gasoline is pumped in at the base of the first tower, flows from its top to the base of the second, and so on, flowing finally as "treated

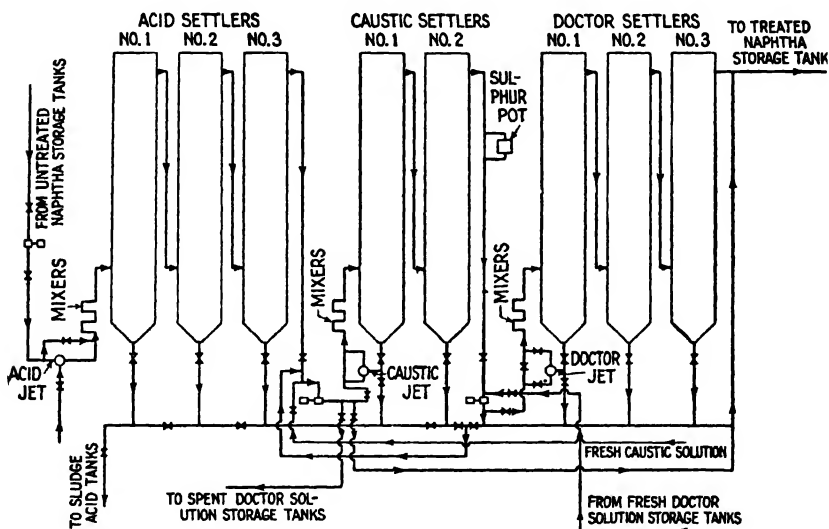


FIG. 103.—Continuous Gasoline Treating Plant. Courtesy The Texas Company, New York City.

stock" from the top of the last tower. The towers are in turn settling and washing towers, the gasoline passing through stationary layers of the solutions. In another type, orifice mixers are used to bring the gasoline and treating liquids in intimate contact, but settling and washing tanks are used as in the previous process. When the acid has been washed out, the gasoline is treated either with caustic soda alone or with the caustic-plumbite "doctor" solution, followed by settling and washing.

If sufficient changes have been brought about by chemical treatment to produce some higher-boiling compounds, the gasoline may be rerun in a shell still heated by steam. In some cases a light treatment, fol-

lowed by steam distillation, the tarry products being left behind in the still, is more effective than heavy treatment with no succeeding distillation.

Knocking. The phenomenon of "knocking" refers to a sudden and violent detonation in an internal-combustion engine cylinder rather than the more steady and gradual burning of the gasoline-air mixture characterizing normal operation of an engine. This takes place particularly under the higher compressions that give added power to the engine. Gasolines differ widely in their tendencies to knock. Straight chain paraffin hydrocarbons are more apt to knock than olefines, whereas naphthenes and aromatic hydrocarbons have the least knocking tendencies. Tests on branching chain paraffins indicate that they do not cause knocking under conditions where straight chain paraffins knock badly. Some crudes produce gasolines that have distinct anti-knock properties, and cracking, particularly by high-temperature methods, results in gasolines that have greatly reduced knocking tendencies. In addition to altering the nature of the hydrocarbons to lessen knocking, producers of gasoline add to their products organic compounds in which lead tetraethyl, $\text{Pb}(\text{C}_2\text{H}_5)_4$, is dissolved. Of a number of organometallic compounds, this substance has proved to be most effective. It is easily manufactured, and is not so expensive as to alter very greatly the selling price of the gasoline containing it. Not more than 0.1% of this substance is necessary to prevent knocking under the conditions under which modern engines are run. The substance is extremely toxic when highly concentrated, but is manufactured with the same safety precautions that characterize the production of many other even more toxic substances, and once in gasoline is a source of very little danger. Those who handle gasoline containing this substance are warned not to allow it to remain on the skin, and to change clothing on which it has been spilled. Gasoline containing lead compounds should never be used in lamps or stoves. The combustion in the motor forms lead oxide, and the amount reaching the air is too small to be a source of danger. In fact, the carbon monoxide from the exhaust of a car is far more dangerous.

Just why one fuel knocks and another does not is not known, nor is the function of the anti-knock compound understood. Some of the theories which have been advanced to explain the latter include: formation of a protective film on minute droplets of gasoline, thus retarding their ignition; furnishing a large number of metallic oxide particles as ignition points and thus causing steadier burning; adsorption of carbon particles on metallic oxide particles and prevention of mist

formation; decomposition of organometallic compounds in drops to give heat to vaporize droplets and thus prevent preignition.

Tests of Gasoline. Some tests applied in the evaluation of gasoline are arbitrary, and few have any chemical meaning. The effect of gasoline on a polished copper strip, the appearance of a polished copper dish in which gasoline has been evaporated, and the quantity of residue left behind constitute tests which gasoline must meet, a good grade producing negligible coloration or residue. Specific gravity has little significance, since it has no relation to volatility except where products from the same crude are compared. Benzol boils at 80.4°C . but has an A.P.I. gravity of 29° . Although distillation tests of gasoline certainly do not duplicate evaporation conditions in a carburetor, since in distillation the composition of the liquid in equilibrium with vapor in the flask changes continually whereas in the carburetor the vapors are in equilibrium with the whole mass of the liquid, standardized distillation tests have been so correlated with actual operating tests that a gasoline may be satisfactorily evaluated by them. Specifications call for a limited amount of material to be volatilized at lower temperatures, only enough to insure starting with a cold engine. Heavier products burn readily when the engine is warm, but no material should be present so heavy as to escape combustion with consequent "carbon" deposits and crankcase dilution.

Casing Head Gasoline. Natural gas carries considerable amounts of volatile hydrocarbons that are capable of existing as liquids at room temperature. If these hydrocarbons are blended with heavier hydrocarbons, the partial pressure of their vapors is sufficiently low that they may be used in such mixtures as motor fuels. There are two general methods of recovering liquid hydrocarbons from gases, compression and absorption. Compression methods are used with relatively rich or "wet" gases and involve compression and cooling with the removal of liquids in traps. Under these conditions such substances as propane may liquefy, but these are generally allowed to vaporize and are returned to the gas. With gases carrying lower amounts of recoverable material, absorption in gas oil is the better method. The compressed gas is washed with gas oil, and the dissolved hydrocarbons are removed with steam in tower stills. The products of both methods are blended with heavier naphtha to enable them to be more safely transported and used without excessive loss by evaporation. Since vast quantities of natural gas are available in this country and much of it has sufficient gasoline to make recovery profitable, casing head gasoline represents a very considerable part of motor fuel supplies.

Kerosene and Furnace Oils. Vast amounts of the petroleum product known as "kerosene" or "lamp oil" are used for illumination in the world, in the rural regions of the more highly developed nations, and especially in Asia and Africa. A great deal of this material is also used in portable and kitchen stoves. A somewhat less volatile material is "furnace oil," which finds very extensive use in house-heating plants. Some oils in the kerosene range may be used in internal-combustion engines, equipped with special preheaters and carburetors.

Flash tests (the temperature at which the oil gives off sufficient vapors to cause a flash of flame) are required by laws all over the world on all lamp oils, the usual minimum being 100° F. Other requirements of lamp oils include freedom from disagreeable odor or marked color, and the ability to burn with a steady flame without smoke and without gumming when used on a wick. Certain hydrocarbons, particularly those lower in hydrogen, tend to gum, and sulfur compounds are objectionable not only because of odor, but because of their effect on the burning qualities of the oil.

The stock from which lamp oils and furnace oils are made comprises straight distillates from crude petroleum, and the less volatile products of cracking. Modern distillation methods with bubble towers have largely eliminated the necessity of redistillation of such fractions.

Products in this range usually require chemical treatment. For the most part this resembles the treatment of gasolines. Some refiners regard acid finishing of kerosenes as bad practice, and either filter or rerun any which require acid. Bell, however, states that from 5 to 15 lb. of sulfuric acid are required per barrel of kerosene. Batch treatment is general practice. The oil and solutions are charged into large covered tanks, which are lead-lined and equipped with a conical bottom. The contents are stirred either by air blast or more satisfactorily by circulating pumps. Since the material is not very volatile, evaporation losses are low, and there is little danger of explosion.

Liquid sulfur dioxide removes aromatic compounds burning with a smoky flame, and is especially adapted to the treatment of oils in the kerosene range. This process is unsuitable for treating gasolines since it removes substances that have very high anti-knock value. If sulfur is quite high, the oil may receive a light sulfuric acid treatment, followed by the use of sulfur dioxide. In general, the procedure with liquid sulfur dioxide includes dehydration, removal of air with vacuum, chilling in double-pipe chillers first with chilled oil and then liquid sulfur dioxide, mixing with the dioxide in packed towers and separation into two layers. The oil layer, after passing through chillers to cool

down the incoming oil, is warmed up by oil from evaporators, heated by contact with steam coils, and is sent into a shell evaporator. Most of the sulfur dioxide is removed at atmospheric pressure and the remainder in vacuum evaporators. The hot oil is brought back to room temperature in heat exchangers. The extract is handled in much the same way, the sulfur dioxide being compressed and liquefied for reuse. The residue from the sulfur dioxide extract makes a good fuel oil.

The uses of materials in this range vary with the specific gravity, lamp oils being of the order of 40° to 48° A.P.I., whereas furnace oils may be as heavy as 38° A.P.I.

Gas Oils. The most abundant product of straight distillation of petroleum is that material which is commonly known as "gas oil." This term arises from its very general use in making "carburetted water gas." It is an excellent Diesel engine and domestic furnace fuel but has no special advantage over crude petroleum as a power plant fuel. It is too heavy for a lamp oil and too light for use as a lubricant. Thus its price occupies the lowest point on the curve of prices of petroleum distillation products as a function of specific gravity. Gas oil, of course, commands a higher price than heavy fuel oil because of its potentialities as cracking stock. A very considerable part of all gas oil thus finds its way into cracking units for the production of gasoline. The residues from such operations may still be used, although not so satisfactorily, in making water gas.

Lubricants. The main compounds present in finished lubricating oil are probably naphthenic or cyclic compounds, primarily polynaphthenes and compounds made up of polycyclic nuclei with paraffin side chains. Along with the high-boiling liquid hydrocarbons there distills from all non-asphaltic crudes a series of paraffin hydrocarbons that form crystals. Some of these compounds crystallize readily when such fractions are chilled. Others are inhibited from crystallizing by substances functioning as protective colloids, by highly viscous liquids, and by the formation of eutectics. These crystalline materials, known as "waxes," not only have no lubricating value, but interfere with the flow of the lubricant at lower temperatures. Modern lubricating requirements, especially in automobiles, are that the oil must not be so stiff at low temperatures as to greatly hinder its movement to rubbing surfaces, nor so thin at high temperatures as to lose viscosity and lubricating power. Further, such lubricants must not be so volatile as to be lost by evaporation from the crankcase, or so unstable as to be decomposed by heat with the deposition of excessive amounts of "carbon."

If the residues left after straight fire and steam distillation through the gas oil range either at atmospheric pressure or reduced pressure contain little or no asphalt, they may be made into steam cylinder lubricants without ever having passed into the vapor phase. Such "steam cylinder stocks" can be made into finished lubricants by carefully regulated "steam reduction," that is, removing more volatile substances with steam, followed by some sort of adsorption process such as filtering through clays. Such lubricants must be blended with tallow oils before they will stick to heated metal surfaces in the presence of steam.

The second method of making lubricants involves their actual conversion to the vapor phase and condensation to a liquid at least once in the course of their manufacture. Even the production of steam cylinder oils by the first method is accompanied by the removal of lower-boiling fractions known as "wax distillate," which material is the source of lighter lubricants and commercial paraffin wax. Distillation of any base oil may be continued until nothing but "flux" or coke remains. Asphaltic base oils are commonly run to flux, and in spite of the rapid increase in use of vacuum pipe stills the running of crude and heavy distillates to coke is still quite prevalent.

The starting material for the bulk of commercial lubricants is the distillate less volatile than gas oil. It may have little or no wax crystals or even "soft waxes," which are probably paraffins dissolved or dispersed in very viscous liquids. On the other hand, this distillate may contain very considerable amounts of these waxes. If the proportion of the soft, non-crystalline wax is high, so that crystals are not readily separated from the liquids to be used as lubricants, it is necessary to subject the oils to redistillation in coking stills. Partial pyrolysis serves to destroy the inhibiting substances and permit free crystallization of paraffin. There are many specifications for different uses, and great flexibility in processing the raw material is necessary to meet these specifications. The higher grades of automobile lubricants are distilled under very low pressures to avoid cracking.

If the lubricant distillate contains appreciable amounts of waxes, it must be put through a process for their removal. If these waxes are crystalline and readily filterable at low temperature, the distillate is chilled, either in vertical cylinders equipped with stirrers and brine jackets, or in double-pipe chillers, the brine flowing in the annular space between the two pipes and the thick mass of oil and crystals being carried forward by a screw conveyor in the inner pipe. Filtration is carried out in plate and frame presses of special type. In these

the cloth is attached by rims and rivets to both sides of circular plates with center grommet feed. These plates are made up of three plates fastened together, the center being solid, and the outside plates perforated. The frames are quite thin, usually $\frac{1}{2}$ in.; and a large number of plates and frames are used, being held together by a powerful hydraulic cylinder. The pressure in such presses is of the order of 350 lb. per square inch. The plates vary from 27 in. to 48 in. in diameter, and as many as five hundred with corresponding frames are in a single press. The oil escapes from the edges of the cloth. The material retained on the filter cloth contains considerably more oil than crystals, and further separation is accomplished by chilling the mixture and slowly warming. The warmth causes expansion of voids between crystals and breaking up of cell structures. By several repetitions of this process, solids and liquids are separated.

Several methods are used for removal of amorphous waxes commonly known as "petrolatum." The oil may be diluted with naphtha, warmed, cooled slowly to 8° to 10° F., and allowed to settle for several days. By the use of high-speed centrifuges the force of gravity may be enormously multiplied. Petrolatum being heavier goes to the outside of the bowl and flows upward, its movement being assisted by the introduction of small amounts of warm water, while clear oil is drawn from the layer nearest the center of the bowl. A jet of warm water flushes the petrolatum from the top of the centrifuge. This is the most widely used of all methods.

The use of modern vacuum distillation equipment is producing large quantities of oils of intermediate viscosity. They cannot be dewaxed by direct chilling and wax pressing; they cannot be rerun by fire without a great loss in viscosity; and they cannot be dewaxed by the centrifuge. The method that has proved successful is to dilute them with naphtha, chill the mixture, add a diatomaceous earth (marketed under the name Filter-Cel), and filter. This removes the mixture of amorphous wax and filter-aid and leaves a dewaxed oil.

Diluting with benzol and chilling has also been carried out by one refinery for some time. The principal advantages of this process are said to be elimination of filter-aid and the consequent difficulty of separating it from petrolatum, and considerable lowering of the temperature differential between the pour test and the temperature that must be attained to secure this test in comparison with the centrifuge and filter-aid methods.

Wax-free lubricants may be improved by the adsorption of coloring matter and other undesirable materials by prepared clays. There

are two general methods of clay treatment, percolation and contact filtration. Percolation involves passing the oil under pressure through a steel shell containing granular fullers' earth. When the clay ceases to give its highest efficiency, it is shifted to more highly colored oils to bring about partial improvement, the oil being sent to fresher material for final treatment. When clay ceases to have any decolorizing and adsorbing value, it is drained, and the oil removed with steam and naphtha. The clay is dried and reburned either in rotary kilns or in multiple-hearth furnaces. Contact filtration includes mixing relatively small amounts of finely divided clay of special grade with hot oil and removing the clay in pressure filters. This has taken the place in some plants of acid treatment, although most adsorption processes are primarily for purposes of clarification.

Instead of attempting drastic dewaxing, some refineries have greatly lowered the pour point of their lubricants by the addition of relatively small amounts of a pure and highly refined hydrocarbon in the lubricant range. For example, addition of 1% of this material (known as Paraflow) lowered the pour point of a lubricant from 30° F. to -10° F. In this way all the desirable properties of wax-containing lubricants at higher temperatures are retained, and their disadvantages at lower temperatures are minimized.

Chemical treatment of lubricants is for the most part washing with concentrated sulfuric acid in batch agitators, followed by washing with water and a little caustic. Sulfur dioxide treatment has considerable use in the treatment of lubricants, particularly transformer and turbine oils. Some crudes containing so-called naphthenic acids require redistillation of the lubricant fractions from caustic soda for the removal of these acids as non-volatile salts in the residues.

Paraffin Wax and Petrolatum. The crystalline material filtered from lubricating oil is refined by processes of selective fusion and adsorption. The mixture of oil and wax is melted and allowed to flow on the surface of water in shallow pans. The level of the water is so adjusted that it just reaches wire screens stretched across the trays. The temperature of the water is lowered by chill coils until the oil and wax set into a solid mass. Water is drained away and the temperature of the room is slowly raised. Oil and lower-melting waxes drain away, leaving a honeycomb of higher melting waxes. By repetition of this method a series of waxes of different melting points can be obtained. Molten wax is clarified by fullers' earth. When finally cast into chilled molds, commercial wax is white and free of oil and low-melting components.

The non-crystalline material separated by settling or centrifuging may be refined by adsorption methods. Petrolatum finds use in compounding insulating materials, as a coating of grains of explosives, and as a vehicle for various medicinals for external application.

Fuel Oils. Very little crude oil is burned directly as fuel oil. Whether it is refined to various products or is simply "topped" until the residue reaches a safe flash point depends not only on the value of the product but on other economic considerations. Very large quantities of Mid-Continent crudes are being topped and burned as fuel oil that might yield excellent lubricating oil, but are not refined because of the limitations of the lubricating oil market as well as limitations on the part of operators of small plants. The heavy residue or flux from continuous stills has high heat value, but can only be handled hot. Such residues, if they are to be used as fuel anywhere except in the refinery, are usually blended with lighter residues from cracking operations. By far the largest source of fuel oil at the present time is the residual oil from cracking processes that has become so deficient in hydrogen that cracking is not profitable. Such "pressure tars" and also topped crudes are often too viscous to be handled readily. By the use of pipe stills operating under pressure the viscosity is lowered and a certain amount of light distillate is obtained. There is an increasing tendency for refiners in the interior, where there is less market for fuel oil, to run to gasoline, kerosene, and coke; but on the coast, where fuel oil is in great demand, it does not pay to crack heavy, unsaturated hydrocarbons, and they are put into fuel oil.

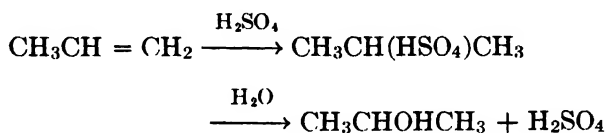
Asphalts. Most petroleum asphalts are refinery residues. They are regarded as being made up of viscous liquid hydrocarbons, amorphous waxes in some cases, together with sulfur compounds, anhydrides, resins, and complex ring compounds with sulfur bridges.

Asphalts from refinery residues may be drawn directly from the still and used as road or roofing materials; they may be reduced with steam over a low fire to certain definite specifications for higher grades for these same uses; or they may be heated and blown with air, or air and steam. Considerable progress has been made in emulsifying with soap and protective colloids, in one process clay being incorporated, thus avoiding heat in their application. Asphalts are also used in paints for the protection of metal and concrete surfaces.

Coke. Petroleum coke is practically pure carbon, and finds ready market in making electrodes and especially in the manufacture of high-grade graphite by electric furnace operations.

Gases. Practically all refinery operations result in the formation of gases or liberation of those already formed. Even storage tanks and agitators yield some gas. These gases carry considerable quantities of condensible hydrocarbons, which are removed ordinarily by scrubbing with an absorbing oil. For the most part, refinery gas is burned in the fireboxes and furnaces of the refinery. In some cases these gases are used, after "reforming" and along with other industrial gases, by public service companies.

Noteworthy progress has been made in the manufacture of alcohols from refinery gases. Since a considerable part of these gases are unsaturated, they may be scrubbed with gas oil and sulfuric acid. The lower olefines, particularly propylene, react to form acid esters which are subsequently hydrolyzed to alcohols. The formation of isopropyl alcohol, which may be regarded as typical, is by these reactions:



This alcohol has about the same physical properties as ethyl alcohol, is non-intoxicating, and may be used for external application as a rubbing alcohol. Large quantities not only of isopropyl but also of secondary butyl, amyl, and hexyl alcohols are now being produced, and are largely used either alone or as esters in the lacquer industry.

CHAPTER XX

ANIMAL AND VEGETABLE OILS, FATS, AND WAXES

Oils and fats of animal and vegetable origin are chiefly composed of glycerides of the higher aliphatic acids. The distinction between a fat and an oil is primarily that of physical condition, and the terms are those that are applied in the countries of their origin. If the material is of semi-solid consistency in the country where it is produced, it is called a fat; if a liquid, it is called an oil.

Substances are called "waxes" that are much harder than fats, possess considerable mechanical strength, and are capable of taking a high polish. Waxes, depending on their origin, may contain fatty acids, alcohols of high molecular weight, esters of these acids and alcohols, and hydrocarbons.

The chemistry of fats and oils is quite complex. None of these glycerides can be fractionally distilled even under reduced pressure, since they are usually decomposed by heat. They do not yield crystalline products, and no fatty oils such as are found in nature have been synthesized in the laboratory. Many individual glycerides have been synthesized, and many fatty acids which have been isolated from fats and oils are well known as to formula and structure. Some have been decomposed into simpler compounds and built up from simpler compounds. There are other acids of which as yet little is known, and concerning whose formulas there is still some doubt. The most complicated factor is that mixed glycerides are the rule rather than the exception. By mixed glycerides is meant the occurrence of two or three different fatty acids in the same molecule. Some of these glycerides contain both saturated and unsaturated acids. Only a few have a preponderance of saturated fatty acids.

A commercial distinction is that of drying, semi-drying, and non-drying oils. Fats and oils whose iodine numbers are below 100 are non-drying; those with a value between 100 and 130 are semi-drying; drying oils have iodine numbers of 130 or above. The term "drying" refers not to evaporation but to a thickening and hardening caused by the oxygen of the air. Those oils that are highly unsaturated take

up oxygen from the air very readily and change from a liquid to a hard, resistant, tough solid. In addition to the main component of fats and oils, namely, glycerides of fatty acids, there are present in all these substances small amounts of resins, pigments, organic phosphorus compounds known as phosphatides, and complex alcohols called sterols. Most fats and oils contain but traces of hydrocarbons. The odor and flavor of fats and oils, whether slight or strong, are due chiefly if not entirely to essential oils or resins.

The tests applied to the distinguishing of these substances from each other, and evaluating them, are more or less arbitrary. This is true because all these substances are mixtures, and furthermore, because the nature of an oil, fat, or wax may vary considerably with seasons and with localities. It is only possible to lay down certain limits within which products of high quality are known to fall, and to require that all products shall conform to those standards. The common physical tests include specific gravity, refractive index, melting point, and titer test (the solidification point of the fatty acids obtained from the sample).

Following are some of the more common chemical tests:

Saponification Number. The number of milligrams of potassium hydroxide required to saponify one gram of the sample.

Iodine Number. The percentage of iodine that will be taken up by the oil in given time under arbitrary conditions. A measure of unsaturation.

Acid Value. The number of milligrams of potassium hydroxide neutralized by the free acids present in one gram of oil.

Acetyl Value. This is a measure of the amount of acetic anhydride that will react with the oil with the formation of acetyl groups.

Reichert-Meissl Number. A measure of volatile insoluble fatty acids derived under arbitrary conditions.

Polenske Number. A similar value involving titration with 0.1 *N* barium hydroxide instead of potassium hydroxide.

VEGETABLE OILS AND FATS

Vegetable fats and oils, depending on their character or quality, are used for either edible or technical purposes.

A. Edible Oils. Edible oils and fats are a highly concentrated form of food. Unlike most other foodstuffs they contain only traces of moisture and no fibrous (roughage) materials. All have approximately the same heat value, and the question of their relative value

for domestic use is largely one of preference. Matters of taste and flavor involve very small amounts of chemical constituents, but are of very great commercial importance.

Cottonseed Oil. The seed, from which most of the fiber has been removed by ginning, is carefully cleaned and is put through a reginning process which removes the larger part of the short fiber from the seed. The linters so obtained are extensively used in chemical processes requiring relatively pure cellulose. The delinted seeds are sent through mills, which serve to break the outer seed coat and free the meats. The hulls are separated from the meats by shaking screens. These hulls have a slight feeding value for cattle, mainly as roughage.

The meats are ground to a fine meal and cooked in shallow vertical cylinders arranged in tiers. This cooking serves to break up the oil cells, to coagulate albumens, and to cut down the viscosity of the oil. The cooked meats are formed into slabs, which are wrapped in hair press cloths, placed on trays, and laid between the plates of a hydraulic press, and a maximum of 4000 lb. per square inch pressure is applied. The oil that runs out is dark red and has a distinctive taste and odor. The pressed cake is ground and used as a fertilizer and as a stock food.

One ton of seed produces about 500 lb. of hulls, 1000 lb. of meal, and 300 lb. of oil. In addition to the hydraulic pressing method a great many modern mills use the expeller mill.

Solvent extraction is not used in the cottonseed oil industry in this country, but many edible oils are produced in Europe by the use of solvents. Extractors may be of the intermittent type, in which the solvent is mixed with the oil-bearing meal and then drawn off, or by a continuous type in which hot, freshly condensed solvent drips through the oil-bearing material and removes the oil by solution. In either case the solvent is removed from the oil by evaporation at relatively low heat.

The crude cottonseed oil is subjected to a refining process. The first treatment is to add a solution of sodium hydroxide to the oil. The concentration and amount used are governed by the quantity of free acid and coloring matter in the oil. The caustic soda solution and oil are mixed together in tanks equipped with stirrers and steam coils. The temperature range is from 30° C. at the start to a maximum of 50° C. After some time, clear oil separates from a brown flocculent precipitate. The contents of the tank are allowed to stand for 24 hours. At the end of this time the precipitate, which is known in the industry as "foots" or "soap stock," is in fairly dense form on the walls and bottom of the tank. It is made up of soap, produced by

the action of the free fatty acids with the caustic soda, coloring matter, albuminous substances, and some entrained neutral oil. If the price of oil justifies, this may be recovered by mixing the soap stock with water and passing it through high-speed centrifuges. The soap stock is used as a raw material for the manufacture of fatty acids, and is also commonly boiled with caustic soda to saponify the neutral oil, the soap separated and partially decolorized by treatment with brine, and mixed with soda ash to make washing powder.

The oil after treatment with caustic soda is a rich golden yellow with a slight reddish tint. If made from a good grade of seed, it is known as "prime summer yellow." The oil still possesses a distinctive taste and flavor. Coloring matter must be removed to improve both taste and flavor. The bleaching process includes adding fullers' earth or a mixture of fullers' earth and activated carbon to the extent of 2% to 6% of the weight of the oil to previously dried oil, agitating the mixture thoroughly, heating to 105°–110° C. for 15 to 25 minutes, and filtering it through a plate and frame press. It is deodorized by passing dry, superheated steam through the oil, which is kept under very high vacuum. This treatment removes both the normal odor of the oil and an earthy odor imparted by clay. Further bleaching accompanies deodorization.

Oil to be sold as a salad oil is subjected to a process known as "wintering." The oil is chilled to 0° C., and the solids, which are mainly palmitic and stearic acids and mixed glycerides of unsaturated fatty acids, are removed by filtration.

Olive Oil. Olive oil is produced by crushing or otherwise disintegrating ripe olives and pressing the crushed pulp. It is always customary to make two pressings of the pulp, and often three are made. Provided clean equipment is used and the olives are sound, the second pressing also yields a fine quality of oil. The crushing equipment commonly used is a chaser or edge runner. Grooved crushing surfaces avoid breaking the pits in order to insure a high-grade oil. A somewhat lower grade is made by grinding the press cake so as to crush the pits, adding hot water, and pressing. Solvent extraction results in a product known as "olive oil foots," which is valuable in soap making.

The expressed oil is not ordinarily subjected to a refining operation, since the flavor is pleasant and should be retained. The oil is settled or filtered, and stored for several months before it is marketed. Lower grades of olive oil may be refined in the same way as cottonseed oil, but the oil must be labeled to indicate that it has been so refined from second-grade material.

Peanut Oil. The meats may be pressed cold, but usually they are heated and pressed hot. Peanut oil is refined in the same way as cottonseed oil.

Corn Oil. Since the germ must be removed from corn before starch can be obtained, the corn germ is utilized as a source of edible oil. The germs are warmed and pressed in expeller mills. The yield is of the order of 1.5 lb. per bushel (56 lb.) of corn. The crude oil is refined very much as cottonseed oil, except for the addition of soda ash to form a solid soap stock. It finds its chief use as a salad oil.

Soya Bean Oil. Soya beans have been grown extensively in this country for a number of years for hay, and the beans were not harvested. At the present time, however, considerable quantities of soya bean oil are used in the manufacture of vegetable shortening, as well as in making soap, paint, and varnish. Soya bean oil is an excellent "core oil," that is, a binder for the sand used as molds in casting metals. In the United States, during the last three months of 1931, 38,803 tons of soya beans were crushed, producing 10,655,357 lb. of oil. The press cake is ground to meal, which is used largely for feeding stock.

Sesame Oil. The oil derived from sesame seed is a widely used food oil in Europe, Asia, and to some extent in Mexico. The finest grades of oil are cold-pressed. Hot-pressed oil must be refined before it is used. In Germany and some European countries from 5% to 10% of this oil is required by law in all butter substitutes, because it can be very easily detected by a sensitive color test.

Cocoanut Oil. Copra, the dried meat of the cocoanut, is ground and heated, and the oil pressed from it, both expeller mills and hydraulic presses being employed. The oil has a very low iodine number, since not more than 10% of the fatty acids present are unsaturated. It also has a very high saponification number, the fatty acids being of relatively low molecular weight. It finds its chief use in making nut butter, margarines, and as a soap oil.

Palm Oil. There are two general divisions of palm oils. Palm kernel oil is very much like cocoanut oil and is made by pressing the palm kernels or seed. What is generally known as palm oil comes from the flesh of the fruit of a variety of palm trees. In addition to the primitive native methods, which for the most part yielded highly acid palm oil, much oil of low acidity is being prepared in modern oil mills. A large part of this oil is refined and used, chiefly in the manufacture of margarine and as a soap oil; large quantities are employed in the quenching vats in tin plate manufacture. At one time palm oil was

considered essential in this process, but its place can be taken by hydrogenated cottonseed oil, as well as other substances of a similar nature.

B. Technical Oils. *Linseed Oil.* The flax plant when grown for fiber does not produce seed that have any commercial value, because the plant is not allowed to ripen before harvesting. When the plant ripens, the seed, often known as linseed, contain large amounts of oil, the average being from 36 to 40%. A good grade of seed will yield as much as 2.5 gallons per bushel. The chief source of linseed is Argentina. In the United States, Montana, Minnesota and the Dakotas are the main producing states. India is third as a producer, and Canada also grows considerable amounts of the seed. Large quantities both of the seed and oil are imported. Linseed oil is made up very largely of glycerides of wholly unsaturated acids of the $C_nH_{2n-2}O_2$ and $C_nH_{2n-4}O_2$ series. When films of linseed oil are exposed to the air, they undergo chemical changes with the formation of a tough, resistant material known as "linoxyn." This phenomenon is referred to as "drying," and it gives oils of this type great value in paints and varnishes. The production of linseed oil is essentially the same process as that for cottonseed oil. The refining method is also very much the same, although some sulfuric acid is used in certain plants. Heating raw linseed oil without addition of any chemical produces the separation as a mucilaginous mass of organic calcium and magnesium compounds, which also contain phosphorus, together with carbohydrates and resins. The term "boiled linseed oil" is applied to linseed oil that has been heated with salts of lead and manganese. The oil does not really boil, since glycerides are decomposed before they produce any appreciable vapor pressure. The function of these salts is that of a catalytic material to hasten the formation of the resistant film.

Tung Oil (China Wood Oil). Tung oil is used in varnishes in connection with pine resin which has been esterified with glycerin. The oil is produced from the seeds of the tung tree, grown very extensively in China. Its cultivation is now being studied in many parts of the world where the climate is subtropical. Thousands of acres of land in the Gulf States are now devoted to growing tung nuts. The largest planting at the present time is in Florida, where a tung oil expeller mill has been in operation for several years. The seeds or nuts are ground and cooked, and the meal is pressed.

Castor Oil. Medicinal castor oil is made from the seeds of the castor plant by cold pressing the meats after the removal of the hulls. Technical grades are the result of hot-pressing or solvent extraction.

The press cake is poisonous and is used only as a fertilizer. Castor oil blended with mineral oil is used as a lubricant for machinery. It also finds a large market in dressing leather, in transparent soaps, and as a softening agent in making artificial leather. It is sulfonated and in this form finds use in lubricant greases and in the textile industry.

C. Vegetable Fats. There are a large number of vegetable fats, commonly known in the trade as "butters" or "tallows." These are obtained chiefly from the seeds of many kinds of trees growing in the tropics. Few of them, however, are used in the United States, the most important being cocoa butter, Japan wax, and Chinese vegetable tallow.

The quantities of these materials produced in this country in a year are not wholly indicative of their importance. Some oils are very necessary to certain industries, and thus have relatively more importance in proportion to amount produced than other oils made in much greater quantity. Following are the figures for vegetable oil production in the United States for 1929:

OIL	MILLION POUNDS	
	Crude	Refined
Cottonseed	1581	1450
Linseed	755	
Cocoanut	352	322
Corn	134	121
Castor	76	
Peanut	16	11
Palm kernel		15
Soya bean	11	8

ANIMAL OILS

Fish Oils. A number of varieties of fish, of which the most important are herring, pilchard, and menhaden, are rich in oil. The usual process is to cook the fish in vats, skim the oil from the surface, and press the cooked fish for the recovery of additional amounts of oil. The press cake is dried and used as a cattle feed or fertilizer. Fish oils are extensively used in dressing leather and as tempering oils in the steel industry. The odor of most commercial fish oils is not pleasant, but by hydrogenation materials are obtained that are entirely satisfactory for soap making and even for food uses.

Fish-Liver Oils. Pharmaceutical cod-liver oil is made by rendering the livers of freshly caught cod. Being rich in fat-soluble vitamins, it is used as a remedy in deficiency diseases. Other fish livers, notably those of halibut, are sources of valuable medicinal oils. Commercial fish-liver oils are used in the leather industry.

Blubber Oils. These come largely from seal, whale, dolphin and porpoise, and are obtained by steam rendering.

Oils from Land Animals. Oils derived from the hoofs of horses, sheep, and cattle find large use in leather manufacture. Egg oils are used for the same purpose. Lard oil, obtained by the pressing of chilled lard, is a most excellent cutting oil, and is also used in signal lanterns. Tallow oil, pressed from chilled tallow, has some value as a lubricant, but the finer grades are used in the manufacture of margarines.

ANIMAL FATS

Butterfat. Butter is a very widely used glyceride, the production in the United States being of the order of one and one-half billion pounds yearly; this is second only to the production of lard. The present tendency in the manufacture of butter is largely towards centrifugal separation of cream on the farm and the production of butter at central manufacturing plants. The cream is churned, either before or after souring, to bring about a separation of butterfat. The quality of butter is very closely guarded by legal restrictions, and adulteration and substitution very largely prevented. Unsalted butter, powdered milk, and water in correct quantities may be mixed, and the suspension forced under high pressure through very fine orifices in order to secure thorough homogenizing. This material functions fully as well as fresh cream in the production of ice cream.

Lard. The finest grades of lard are made from certain selected portions of hog fat by heating the fat to a maximum of 50° C., removing the liquid, and chilling it suddenly in brine. This material is largely used in making oleomargarine. The ordinary grade of cooking lard is obtained by heating the fat, cut from all portions of the animal, in closed kettles at 40 to 60 lb. steam pressure. The residues left after steam rendering are run through expeller mills to recover further quantities of glycerides which are choice greases. The production of lard in the United States is something of the order of two and one-half billion pounds per year, making this the most widely used of all glycerides.

Tallow. This term refers to a product made from the natural solid fat of beef and mutton. Edible grades of beef tallow are melted and then held in a constant temperature room until the higher-melting glycerides have separated by crystallization. These are removed from the liquid by filtration and pressing, the whole process being known as "graining." The solid fraction is called "oleostearine," some of which is used in lard compound. The filtrate constitutes the "oleo" oil, which is used in oleomargarine. Commercial tallows are obtained by rendering under pressure. These find use in making soap, and as a constituent of certain lubricants.

WAXES

Carnauba Wax. This wax is a coating on the leaves of the South American Carnauba palm. It is scraped off and melted in boiling water. The product in refined form is a light yellow solid, used in making floor waxes, candles, and phonograph records.

Candella Wax. The leaves and stems of a plant growing in Southern Texas and Northern Mexico are covered with waxy scales. The stems are harvested, and the wax removed by boiling water. It is refined by remelting with clean water, and may also be bleached to meet specifications. It has much the same uses as carnauba wax.

Beeswax. Honey comb is melted in hot water, steamed, and pressed for the manufacture of beeswax.

Spermaceti. The blubber oil of sperm and bottle-nose whales may be chilled, filtered, and the cake pressed for the final removal of oil. The solid residue after refining consists chiefly of cetin, or cetyl palmitate, along with minor quantities of other esters and free alcohols. Spermaceti is used largely in the manufacture of cosmetics.

Sperm Oil. This material, derived from the head cavities of sperm and bottle-nose whales, is chemically a wax, but has all the physical properties of oils. It is used in the leather industry and as a lubricant.

Shellac Wax. In the manufacture of commercial shellac, a by-product (wax) of some commercial importance is produced.

Lanolin (Wool Fat). The oily substance removed from raw wool by the use of warm soapy water by solvents may be refined into the form of a soft, white, semi-solid material resembling animal fats. It is marketed under the name of "lanolin." This substance has definite healing properties, and also may form smooth and stable emulsions of a thick creamy consistency containing as much as 50% water. Hence lanolin finds very extensive use in preparing all sorts of ointments and

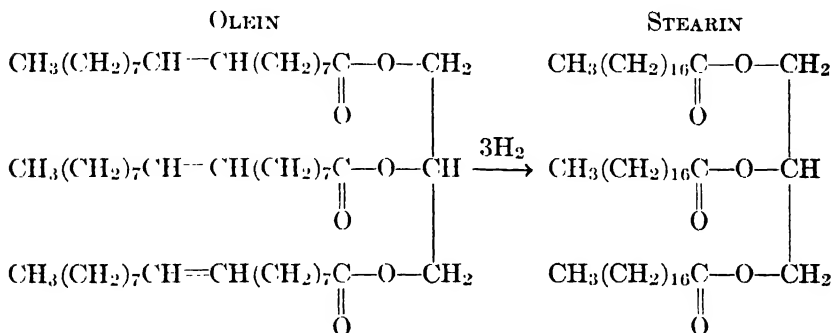
face creams. Water-soluble materials may be incorporated in it, and the emulsion retains all the desired physical properties of an ointment. The chief components of lanolin are sterols, the most important of these being known as cholesterol.

PRODUCTS OF OILS AND FATS

In addition to being used directly, many of the materials just described are subjected to chemical treatment in order to produce several necessary and valuable articles of commerce.

Hydrogenated Oils

Examination of a typical unsaturated glyceride, olein, shows three points of unsaturation. The addition of six atoms of hydrogen to the three double bonds will produce stearin, which is a solid at ordinary temperatures.



The treatment with hydrogen produces profound physical changes and also renders the substances much less sensitive to chemical changes. While the main reasons for hydrogenating oils is that people in cooler climates are accustomed to lard as a shortening and cooking fat, this may be regarded as purely an esthetic reason. Oils that are hydrogenated do not become rancid so readily; they do not absorb odors; and the process of adding hydrogen largely removes tastes and flavors that render them either inedible or unfit for use in making soap. Hydrogenated oils produce harder soaps than do the untreated oils.

Although platinum and palladium are most efficient catalysts, they are expensive and easily poisoned. Finely divided nickel is most widely used in catalytic hydrogenation. The catalyst is commonly prepared by distributing nickel oxide on the surface of inert material

and reducing this oxide by hydrogen at a relatively low temperature. The catalyst is reduced while in suspension in oil to prevent contact with the air. Hydrogen is obtained largely by electrolysis of water, since purity is of prime importance. The catalyst is carefully protected from the action of such poisons as sulfur, chlorine, phosphorus, arsenic, and carbon monoxide. Air and water are rigidly excluded. The reaction between unsaturated glycerides and hydrogen is exothermic, and provision is made for removal of this heat and control of temperature. The hydrogen may be used at atmospheric pressure, or up to a maximum of 80 lb. Temperatures range from 250° C. at

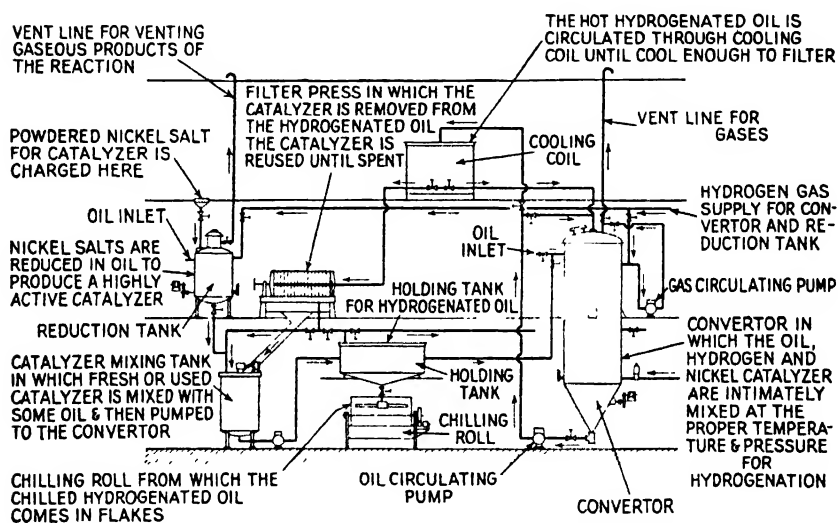


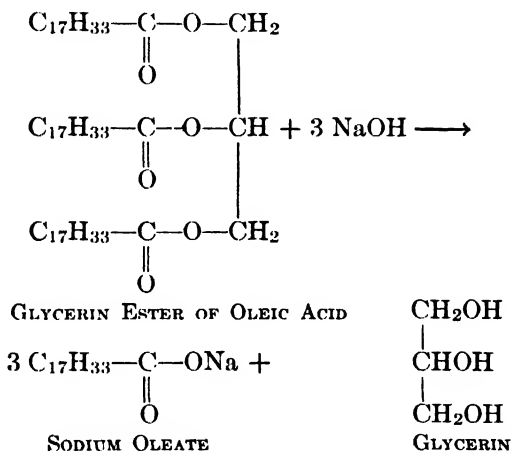
Fig. 104.—Hydrogenation Plant Courtesy Wurster and Sanger, Inc., Chicago, Ill.

atmospheric pressure to 170° C. with hydrogen at 80 lb. pressure. The catalyst, which varies in amount from 2 to 6 lb. per ton of oil, is kept in suspension either by stirring with hydrogen or by mechanical stirrers. Unchanged hydrogen is returned to the process until the reaction has proceeded to the desired point. Inert gases are vented. Most common practice is to hydrogenate to a definite melting point and consistency, although some small plants buy highly hydrogenated material and mix it with oil to make vegetable shortening. The catalyst is removed by filtration, so that only minute traces remain in the oil. The process is controlled largely by the iodine number. Hydrogenated products are best detected by tests for nickel in the ash. The amount present in ordinary hydrogenated oils has no physiological effect, being less than

that found in foods cooked in nickel-lined vessels. Although hydrogenated oils are extensively used in making soap, their chief importance is in the production of cooking fats and butter substitutes. Their melting point must be below body temperature to make them fit for use as a food.

Soap

Any metallic salt of a fatty acid is technically a soap, but in general the term soap refers to sodium and potassium salts of fatty acids. As a simple example of saponification, the reaction between the glycerin ester of oleic acid and sodium hydroxide may be taken.



Whether or not the glycerin is recovered in the manufacture of boiled and settled soaps depends largely upon the selling price of glycerin. A few large plants regularly recover glycerin most of the time regardless of price unless the stocks on hand become too excessive.

Potassium hydroxide is the chief base in soft soaps, but caustic soda finds a very much larger use in the soap industry in general. The consistency of the soap depends both on the chemical nature of the fatty acid and on the method of manufacture. Partially or wholly refined fats and oils, and hydrogenated oils, find use in the soap industry. Laundry soaps of the cheaper grades also contain the sodium salt of abietic acid, $\text{C}_{19}\text{H}_{28}\text{O}_2$, derived from the action of alkali on pine resin.

The oil or molten fat is run into very large kettles along with a dilute solution of caustic soda to produce emulsification. The kettles range in size up to a maximum of 80 ft. deep and 30 ft. in diameter.

Later a more concentrated caustic solution (12 to 13%) is added, the glycerides being maintained in slight excess. The mixture is heated by steam to a point where reaction begins, after which the heat of reaction will keep the contents of the kettle boiling. Saponification is carried to the desired extent by the addition of small amounts of caustic soda in successive portions. Soap will form a colloidal jelly with water, which would prevent its removal from the kettle. The soap is coagulated in the form of a relatively firm mass by the use of brine or excess of caustic soda. The brine is prepared by adding dry salt to the contents of the soap kettle. After several days' standing the soap separates into an upper layer of light color and good grade, and a dark layer known as "niger," which is used again in later processes, both layers floating upon the solution of sodium chloride and glycerin. Rosin soap is made either by boiling lump rosin with soda ash, or by adding rosin to caustic soda in a kettle containing ordinary or tallow soap.

The soap produced by any process is sent to heated storage tanks and thence to mixing vessels known as "crutchers." A considerable variety of materials are incorporated into soap, depending on the use to which the soap is to be put. These include soda ash, sodium silicate, borax, starch, abrasives, colors, and common perfumes. Floating soaps are made by running the crutcher at high speed and reversing the paddles at intervals to beat air into the soap. The thoroughly mixed soap from the crutcher is placed in narrow boxes with removable sides, which are set on low trucks. After standing for a day the soap is sufficiently hard to stand alone. These slabs are usually about 1 ft. thick, and 5 ft. by 6 ft. in area. They are cut by horizontal and vertical wires into bars, the bars are dried in tunnel driers until a skin forms on the surface, and are then pressed into final form. A variation of this process is employed in the making of the high-priced grades of soap. The materials used in the kettle are very much the same, but the soap is sent from the kettle on a belt through a drying chamber. The dry soap is mixed by the use of corrugated rolls with colors, fillers, and fine perfumes. It is then forced by a heavy screw through a die in the form of a bar, which is cut and pressed into final form into molds.

Among the special types of soaps are soft soaps, made with caustic potash and oils high in oleic acid; liquid soaps, made by adding glycerin and alcohol to the soap; transparent soaps, produced by dissolving soap in alcohol, decanting from insoluble material, and removal of the excess alcohol by distillation; shaving soaps, which contain potash soap

as a base, together with oils, stearic acid, gums, and various pharmaceuticals; and soap powders, which are essentially soap with an excess of sodium carbonate.

Soap functions as a cleansing agent by virtue of its power to produce an emulsion of oil particles; by acting as a peptizing reagent, causing dirt to assume the colloidal state; and by virtue of foam formation, which seems to lift dirt mechanically from the surface.

Sodium and potassium soaps are of primary importance, but other "metallic soaps," or the salts of a number of metals such as zinc, lead, magnesium, and aluminum with the common fatty acids, find some use in industry. In addition to metal soaps, bases such as the ethanolamines can be used with fatty acids to make soaps which are of high value as emulsifiers, thickeners for lubricants, and cleansing agents. The property of solubility in organic solvents possessed by certain soaps renders them very valuable in "dry cleaning" operations.

Fatty Acids

Fatty acids constitute an important by-product of animal and vegetable fats and oils. They may be produced in the following ways:

1. The residues from the refining of cottonseed oil and other oils with caustic soda, known as "foots," are treated with sulfuric acid to free the fatty acids from the soap.

2. Fats may be hydrolyzed at 250 lb. pressure in an autoclave with such reagents as lime, magnesia, and zinc oxide in the presence of zinc dust.

3. An enzyme prepared from castor beans functions as a hydrolyzing agent, the process being essentially a fermentation.

4. A very widely used process, successfully employed with garbage greases as well as with better grades of fats and oils, employs as catalyst benzenesulfostearic acid, which is probably $C_{17}H_{15}COOC_6H_5SO_3H$, and is known as Twitchell's Reagent. It is made by heating together the fatty acid, benzene (or other aromatic hydrocarbons), and sulfuric acid. The process, which is used mainly with fats, involves a preliminary refining with steam and sulfuric acid. To the fat and about half its weight of water is added the hydrolyzing agent to the amount of 2% of the weight of the fat together with a little sulfuric acid. The mixture is boiled with live steam in copper-lined vats until hydrolysis is 85% to 90% complete. If carried much further, equilibrium would be reached because of esterification of fatty acids by glycerin. The glycerin solution is removed, and after neutralization by lime, filtra-

tion, concentration to 20° Bé, and a second filtration, the crude glycerin is subjected to the ordinary distillation method for the production of commercial glycerin. The fatty acids together with unhydrolyzed fat are boiled with fresh water, reagent, and acid until no glycerides remain unchanged. The very dilute glycerin so made is added to the next run instead of water.

High-grade fatty acids are merely chilled and pressed, the process being repeated two or three times. Lower-grade material is distilled in a cast-iron still heated either by direct fire and by superheated

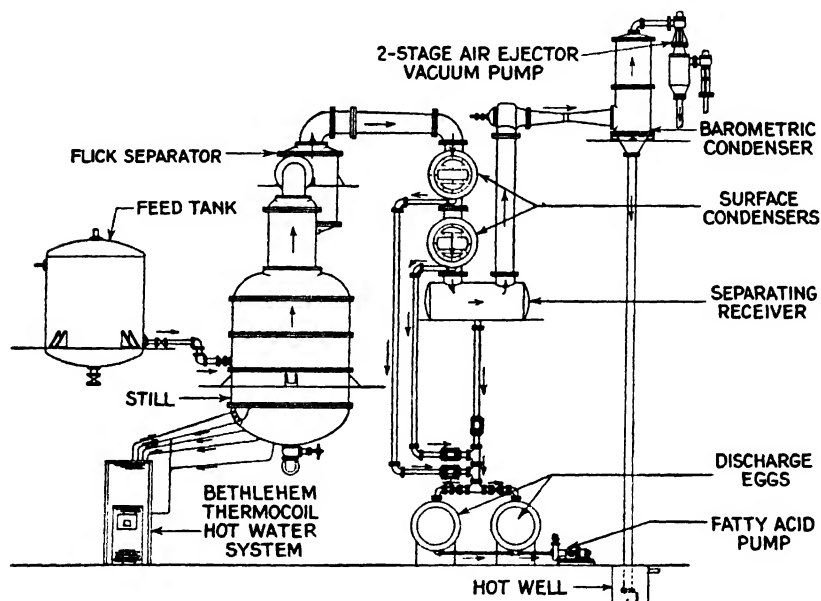


FIG. 105.—Fatty Acid Plant. Courtesy Wurster and Sanger, Inc., Chicago, Ill.

steam admitted into the still or by hot water coils in the evaporator shell. The fatty acids are removed from the steam and gases by copper drums, which function as partial condensers. Water jet barometric condensers for the steam and double impeller exhausters for the fixed gases produce a relatively high vacuum. Crude fatty acids are continuously fed to the still as distillation continues until sufficient tar accumulates to affect the purity of the distillate. These residues are run into other stills, a "black acid" distillate being removed and mixed with ordinary crude acids; a heavy material known as "stearine pitch" remains which is used in much the same way as petroleum, asphalt, and coal-tar pitch.

The distilled fatty acids are chilled; the chilled cakes are wrapped in cloths, and subjected to pressures of 3000 lb. By repetition of this process the liquid acids are separated to a sufficient extent that the solid acids, which have a melting point of a little over 69° C., may be pressed without wrapping and while warm. The last oil pressed from them contains considerable amounts of solid acids and is reworked.

The production of mixed solid acids in the United States in 1928 was around 44,000,000 lb., and that of the liquid acids slightly less. The solid acids find use in candles, polishes, as softeners and carriers of pigments in rubber compounding, as ingredients in cosmetics and pharmaceuticals, and in making metal soaps. The liquid acids are used in the soap, paint, textile, and leather industries. The solid acids bear the trade name of "stearic acid," though those made from many vegetable oil soap stocks contain little or no stearic acid. In the same way the liquid acids are called "oleic acid," although several other fatty acids are present.

Glycerin

Glycerin can be made on a commercial scale by fermentation of carbohydrates, but on account of the present low price of glycerin the process is not in operation. Glycerin is derived practically entirely from saponification of natural fats and oils, being a by-product of both soap and fatty acid manufacture. Glycerin ($\text{CH}_2\text{OH}-\text{CHOH}-\text{CH}_2\text{OH}$) is an alcohol and can produce a large variety of esters. Its nitric acid ester, erroneously called nitroglycerin, is a component of a number of high explosives. Glycerin also finds extensive use in the pharmaceutical industry. It is odorless, possesses a sweet taste, is relatively non-volatile, chemically quite stable, and when cold mixes in all proportions with water. It is also used rather extensively as an anti-freeze for automobile radiators. "Soap lye crude" glycerin, obtained from the brines used to grain soap, contains all the impurities of the soap, some unchanged caustic soda, and salt. It is treated with hydrochloric acid to neutralize excess caustic and ferric chloride, which gives voluminous precipitates of ferric hydroxide and also serves to coagulate colloid matter. After filtration, excess of iron is removed by the addition of the correct amount of caustic soda, followed by second filtration. The glycerin solution still contains salt and the sodium salts of volatile fatty acids. It is sent to multiple-effect evaporators equipped with salt boxes and brought to an average concentration of 80% glycerin. Mineral salts are present to the extent of 8% to 10%.

Saponification crudes are obtained from the fatty acid industry, the

solution being relatively free from salt and other mineral matter. Treatment with small amounts of lime or alum serves to remove impurities. The clear solution is subjected to multiple-effect evaporation, the product being an 88% solution, which gives a very light ash and is practically free from chlorides.

Pure glycerin is obtained by distillation. Since it decomposes at its boiling point to a slight extent with formation of the unsaturated aldehyde acrolein, $\text{CH}_2=\text{CH}-\text{CHO}$, it is best refined under reduced pressure. The technology of glycerin refining comprises essentially a

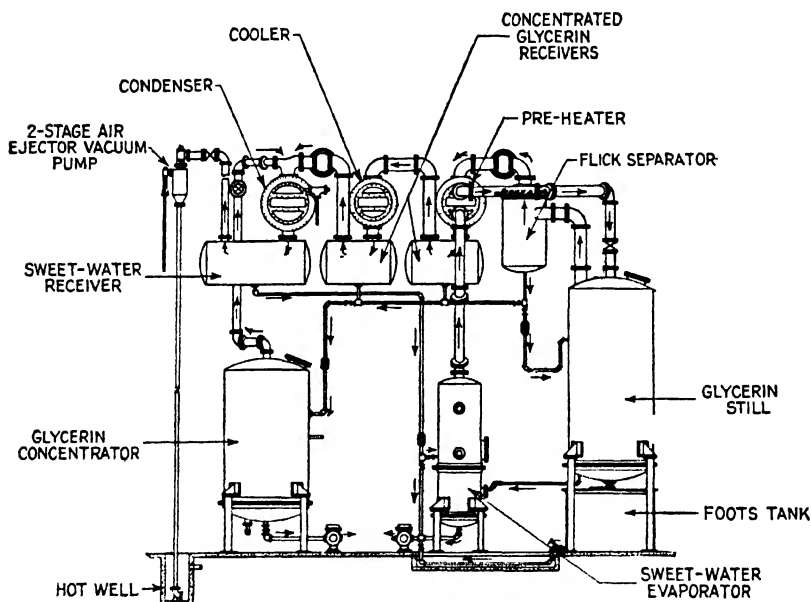


FIG. 106.—Glycerin Distillation Plant Courtesy Wurster and Sanger, Chicago, Ill.

history of the art of distilling high-boiling liquids. Direct heat and air condensers were first used. The next step was the adding of steam to aid distillation. Superheated steam, which had passed through coils exposed to the direct fire under the still, was next used. Vacuum and steam distillation together with evaporation of the final water condensate (known as "sweet water" since it carries appreciable amounts of glycerin) comprised the next step. The final development was the use of high-pressure steam instead of a direct fire to heat the contents of the still. Fractional condensers, which serve as heat exchangers, remove most of the glycerin from the vapors, the remainder being obtained along with the water in surface condensers. The vapors

from the sweet water evaporators are the source of a larger part of the steam used in the process.

The glycerin used in the drug trade is either the highest quality of single-distillate material or is a double-distilled product, and is 95% glycerin. The requirements for dynamite glycerin used in making glyceryl trinitrate (nitroglycerin) are exceptionally rigid. The product must not contain more than 0.01% salt and not more than 0.1% ash. This freedom from chlorides is essential because of the effect of hydrochloric acid in the nitration of glycerin.

CHAPTER XXI

CARBOHYDRATE INDUSTRIES

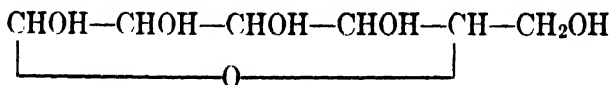
The term "carbohydrate" refers to a series of compounds whose general formula is $C_xH_{2y}O_y$, in which x and y have the same value or different values. In the earlier years of organic chemistry these substances were regarded as hydrates of carbon of the formula $C_x(H_2O)_y$. The simpler members of this series are sugars, and the more complex substances are starch and cellulose. The whole field of carbohydrate chemistry is one which is already of very great commercial importance, and one in which there are unlimited future possibilities. Since practically all carbohydrates are of vegetable origin, raw materials are continually producible. Some carbohydrate industries involve very few chemical changes, whereas others are concerned with profound and thoroughgoing chemical transformations.

SUGARS

The monoses are as yet of limited importance in industry, and only one diose is produced on an extensive scale. No trioses are articles of commerce.

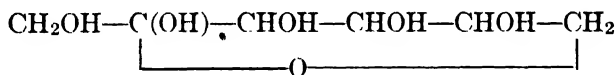
Dextrose (Corn or Grape Sugar). The substance known to the organic chemist as "*d*-glucose" does not bear this name in industry, because of the fact that "glucose" is a term applied to a syrup made by the partial hydrolysis of starch, which contains in addition to this sugar other substances in considerable amounts. Dextrose is found in the juice of grapes, and is often called "grape sugar." It rotates the plane of polarized light to the right, and the name "dextrose" is therefore applied to it.

Dextrose has the empirical formula $C_6H_{12}O_6$, and in the presence of certain reagents it behaves as an aldehyde. It may be regarded as having the formula



Dextrose is produced in quantity by chemical means by the action of dilute hydrochloric acid on a suspension of starch under pressure. The extent to which hydrolysis has taken place is determined by iodine color tests, which show when all starch has disappeared, and by the use of alcohol, freedom from turbidity in this solvent indicating the disappearance of products of partial hydrolysis. Neutralization of free acid by sodium carbonate leaves sodium chloride, an entirely unobjectionable substance, in small amounts in the finished product. The liquid from the converters is concentrated in vacuum evaporators. A crystalline sugar called "cerelose" is made from the concentrated syrup from the vacuum pan. The product has the formula $C_6H_{12}O_6 \cdot H_2O$. The unfounded prejudice against "glucose" and "corn sugar" is gradually disappearing. It should be realized that the first step in the digestion of sucrose is its hydrolysis to dextrose and levulose. There are many food products in which the sucrose has already been changed to dextrose and levulose.

Levulose (Fruit Sugar). The sugar commonly occurring in fruits is called "levulose" because of its rotating the plane of polarized light to the left. It has the empirical formula $C_6H_{12}O_6$, but reacts as a ketone rather than an aldehyde. It is regarded as being either a propylene or amylen derivative. When alone it is probably

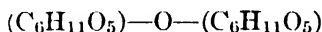


but when present in the sucrose molecule it is probably a 2,4 derivative. The researches of the Bureau of Standards of the United States Department of Commerce have shown that the Jerusalem artichoke can be used as the source of levulose, and some progress has been made towards developing a new sugar industry from this source. The hygroscopic nature of this sugar may seriously limit its industrial development.

Xylose (Wood Sugar). In many fibrous materials there are found complex carbohydrates called "pentosans," since they yield on hydrolysis five carbon sugars. It has been shown by the laboratory and semi-works scale researches of the Bureau of Standards that cottonseed bran on hydrolysis yields around 30% of its weight as pure xylose. Biological chemists regard xylose as having no food value. It has a sweet taste, and probably does no more harm in the digestive tract than cellulose, which is present in considerable quantities in

wheat bran and vegetables. Xylose is not as yet a commercial product, but gives some promise of value as an industrial chemical.

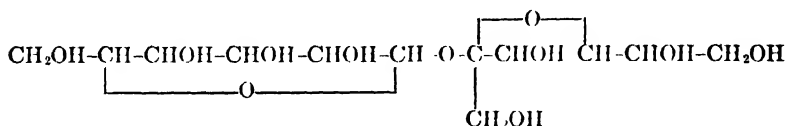
Maltose (Malt Sugar). The diose called "maltose" or "malt sugar" has the empirical formula $C_{12}H_{22}O_{11}$, and is known as a semi-reducing sugar, functioning with reagents as if it had a single free carbonyl group. It is regarded at present as being made up of two dextrose molecules which have lost a single molecule of water, or



It may be made commercially by the carefully regulated hydrolysis of starch, but it is more generally produced on large scale by the action of the enzyme maltase on starch. Maltose is used as a food for infants and as an ingredient of syrups.

Lactose (Milk Sugar). The sugar derived from milk of mammals is called "lacto-e" or milk sugar. It is a diose of the formula $C_{12}H_{22}O_{11}$, and is of the semi-reducing type. Its configuration differs from that of maltose not only in the arrangement of hydrogen and hydroxyl but also in the carbons linked by oxygen. It is made in small quantities for the use of physicians, but is not an important article of commerce.

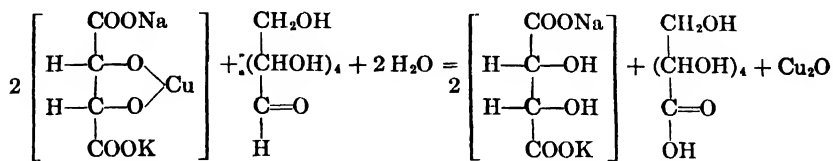
Sucrose (Cane Sugar, Beet Sugar). The diose known as sucrose, $C_{12}H_{22}O_{11}$, is a non-reducing sugar. On hydrolysis it yields equimolecular quantities of dextrose and levulose. It is regarded as having the structure



This breaking up into dextrose and levulose is called "inversion," and an equimolecular mixture of the two sugars is called "invert sugar." Sucrose is very soluble in water, forming syrups. In a sense, sucrose is not crystallized from solution, but separates from a molten mass, the melting point of the sugar having been lowered by the presence of water.

The common analytical methods for control and evaluation of sucrose in the various stages of its production are mainly physical. The only chemical method that has general use involves the action of invert sugar on the copper tartrate complex present in Fehling's solution. Assuming that both dextrose and levulose have a free carbonyl group in the presence of reagents that will react with this group, the

following type of reaction may be regarded as representative, although the reactions are quite complex and vary with conditions.



The cuprous oxide formed may be weighed directly, or the copper in the precipitate determined by any analytical method for copper or standard Fehling's solution may be titrated with sugar solution. An analysis of a mixture of sucrose and invert sugar is possible by determining the invert sugar by this method on one sample, and then after inversion of the sucrose by finding out the total amount of invert sugar. The difference between the two values gives the invert sugar produced from sucrose.

Physical methods include specific gravity of solutions, this being given in "degrees Brix," which refers to percentage of apparent solids in terms of sucrose, and the two optical methods in which the refractometer and polariscope are used. The index of refraction of sugar solutions varies in a regular way with the concentration of the sugar, and where no considerable amounts of dissolved substances other than sucrose are present, the refractive index is an accurate measure of the amount of sucrose.

The ordinary form of polariscope with one fixed nicol prism and one rotating so that the angle of rotation can be measured is not generally used in the sugar industry. Instead, the analyzing prism is also fixed, and the rotation of the sugar solution is compensated by a series of sliding wedges of dextro-rotatory or laevo-rotatory quartz. White light of considerable intensity is used instead of monochromatic light. When an arbitrary weight of sample is used, the reading is directly in percentage of sucrose or "degrees Ventzke" ($^{\circ}\text{V.}$). Various devices are employed to get the end point of uniformly illuminated fields, the amount of light being intermediate between maximum and minimum. The usual instrument has a field vertically divided into two sections. When invert sugar is present, the method of determining sucrose is to take a reading on the sample directly, and then after inversion to make a second reading, allowing for dilution. The amount of change being known, the ratio of the difference in the two corrected readings to that of pure invert sugar at a given temperature gives the amount of sucrose present.

The two main sources of sucrose are a variety of jointed cane known as "sugar cane," and a species of beet. The methods of producing sucrose from the two resemble each other in a general way. Both include obtaining a clear juice, evaporating this to a heavy syrup containing crystals, allowing the syrup to crystallize completely, and separating the liquids from the crystalline material by centrifugals and dryers.

(a) *Cane Sugar.* Sugar cane is a grass with blades spreading from a jointed stalk. It is grown successfully only in tropical and semi-tropical countries, which excludes most of the United States. When

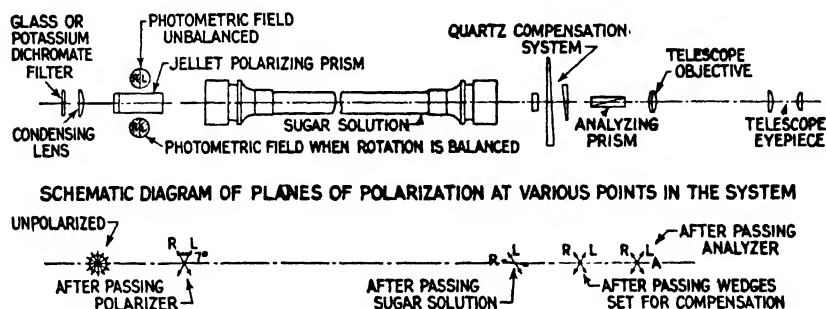


Fig. 107.—Principle of the Saccharimeter. Courtesy Bausch and Lomb Optical Company, Rochester, N. Y.

the stalk is sufficiently mature, it is cut close to the ground after removal of the blades, trimmed from the top down to the nearest mature joint, and the stalks hauled to mills. The stalk contains about 14% of sugars, mainly sucrose, this being approximately the same weight as the dry weight of fiber in the stalk. Most of the rest of the stalk is water.

The cane first passes through crushers, which serve to break up the stalks into a mass of fiber with the extraction of 40% to 70% of the juice. Modern swing hammer shredders and revolving cane knives have also found extensive use in this industry. These do not separate the juice from the cane. The juice is squeezed from the fiber by a series of rolls, each mill being made up of three rolls whose axes are at the apices of an equilateral triangle. After passing through at least two mills, the mass of fiber is wet with water, which is again squeezed out, carrying with it juices not removable by a single mill. As many as seven mills may be set in series, but the usual number in modern factories is five. From 96% to 98% of all sugars shown by analysis to be present in the cane are removed by this treatment. Although

there is an increasing demand for the residual fiber or "bagasse" for making heat-insulating and sound-deadening wall board, most of it is burned as fuel in the power plant of the mill.

The juice is strained to remove fine fiber, but still remains cloudy with suspended matter. It is necessary to remove undesirable materials of a colloidal nature, which would interfere with crystallization of sugar and render it unfit for use as a food. (All methods depend on attaining a certain hydrogen ion concentration in the juice and the formation of precipitates that absorb colloids and mechanically remove them. It is especially necessary to maintain low alkalinity with cane juices because of the sensitiveness of reducing sugars in alkaline solutions.) Organic non-sugars include acids, salts, pectins, celluloses, proteins, gums, aromatic ethers, coloring matter, and living organisms. The most generally used method is to add calcium hydroxide to the juice to faint alkalinity. Any free acids are neutralized and colloids are coagulated and precipitated largely by adsorption by the insoluble lime salts. After heating to or nearly to the boiling point, clear liquid is removed by decantation and filtration or by thickeners. The solids are washed with water to prevent excessive sugar losses. In order to produce a greater amount of precipitate, lime may be added in excess, followed by the use of carefully regulated amounts of such weak acids as carbonic and sulfurous, which cause the formation of insoluble calcium salts. Both acids are introduced in the form of their gaseous anhydrides. Coagulation by these two methods involves heating the juice sometime during the treatment. Sulfurous acid (the sulfitation process) also serves to cut down the color of the sugar ultimately obtained. (The use of phosphoric acid is also of importance in the sugar industry, since it has been found that juices that do not naturally contain a certain minimum of phosphate do not clarify well.) The defect may be corrected by the addition of soluble calcium or sodium phosphates.

The first evaporation is carried out in multiple effect evaporators, which handle not only juice but also all washings and dilute sugar solutions of every sort obtained in the whole process. A concentrated syrup is produced in the multiple effect evaporators, the liquid containing from 55% to 65% solids.

The syrup is fed as needed into a single calandria type vacuum pan using exhaust steam and equipped with "save-all" and barometric condenser. The level of liquid gradually increases as evaporation proceeds. By regulating temperatures and pressures by means of feed of syrup, amount of steam entering each coil, and rate of flow of

condenser water, it is possible to produce tiny crystals of a sufficient number that they will serve as nuclei for further crystallization. The size and hardness of crystal are subjected to control both by the purity of solutions and by manipulation of pressures and temperatures. When evaporation is sufficiently complete, that is when the contents of the vacuum pan are of a gravity corresponding to 93% "apparent total solids," these being either in the form of a solution or crystals, the pan is emptied into a mixer provided with stirrers to keep the crystals from settling.

The thick mixture of syrup and crystals known as "massecuite" is fed from the mixer as required into a series of slowly moving centrifugals until each has received its proper charge. A few minutes of running at around 1200 r.p.m. throws off most of the syrup. In making raw sugar, the crystals are washed as little as possible in the centrifugal because this dilutes the molasses film and endangers the keeping qualities of the sugar. Only enough water is used to bring the sugar up to the desired polarization. All washings are returned for evaporation until sufficient colloidal and inorganic impurities and invert sugar accumulate to render recovery of further sugar unprofitable. Crystallization of low-grade mother liquors cannot be completed in the vacuum pan, but requires the transfer of the pan contents to crystallizers, which are horizontal tanks equipped with stirring blades, and often partially jacketed for steam heating. Crystallizers may be open, or they may be closed to permit the use of a partial vacuum.

What is known as "final molasses" in the sugar industry is a thick viscous liquid from which no more sucrose can be profitably extracted. It also contains reducing sugars, some organic non-sugars, inorganic salts, and water. Final molasses is too highly colored and flavored to be palatable, and is either used in mixed stock feeds or fermented to make industrial ethyl alcohol. Various grades of molasses are used as a food, and these are by-products in the manufacture of raw cane sugar and the refining of cane sugar. Such materials contain much more sucrose and much less of the other substances mentioned above. Table syrups are not by-products of cane mills, but are made by other processes.

Unless the sugar is to be stored for some length of time or shipped great distances, as for example from Australia to Europe, it is not necessary to use dryers in a sugar mill. When drying is necessary, the crystals from the centrifugals are sent through rotary dryers equipped with inner blades and heated by air passed over steam coils.

The product of the centrifugals is known as "raw" sugar, is yellow

to light brown in color, and contains around 97% sucrose, together with some invert sugar and minor impurities. It has a distinctive flavor and finds some use in this form, but most of it is sent to a refinery to be made into very pure sucrose.

(b) *Beet Sugar*. As a result of intensive botanical research the sucrose content of the "sugar beet" has been raised to double its original average value. In addition to sucrose, water, and fiber, there are present, in the sugar beet, raffinose, more complex carbohydrates, and minor quantities of acids, proteins, purine bases, phosphatides, and inorganic salts.

The beets, after washing, are cut by sharp knives into V-shaped slices known as "cossettes," as few cells being ruptured as possible. Under the influence of hot water the protoplasm of the cell coagulates, the cell walls become quite permeable, and sugar is readily extracted. The cossettes are packed into vertical closed cylinders of about 200 cu. ft. capacity known as diffusers, which are arranged in batteries. Fourteen diffusers operating as a single unit, eleven of them being maintained in circulation at one time, will handle from 600 to 2000 tons of beets in 24 hours. Water warmed to about 60° C. is fed to the battery, and is heated during its passage to a maximum of 75° to 80° C. by the direct injection of steam, or by being sent through heaters located between diffusers. Extraction is counter current, the diffuser last charged being the last one in series to receive the extracting liquid. The amount of water used is approximately one and one-half times the weight of the beets.

The pulp removed from the diffusers, even after draining, contains about 95% water. It is either fermented in outdoor silos or pressed to about 85% water content and dried in rotary hot air dryers to 10% to 20% moisture content, both processes resulting in cattle feed. Beet molasses is sometimes mixed with the dried pulp.

The juice is strained and clarified by the double carbonation process, which includes addition of lime and passage of carbon dioxide through the solution at 80° C. The solution is left fairly alkaline in order to get better separation of impurities, and the precipitates are removed by filtration or thickening. The clear solution is again treated with carbon dioxide until precipitation and removal of lime are practically complete. The effects include lowering hydrogen ion concentration, coagulating by electrolytes, formation of insoluble calcium compounds, decomposition of organic bases, and adsorption of undesirable material by the calcium carbonate. Tricalcium saccharate may be used instead of lime, being decomposed by carbon dioxide into

calcium carbonate and sucrose. Considerable frothing attends carbonation, and in some cases mechanical devices are supplemented by the use of small amounts of vegetable oils. In order to produce a white sugar, carbonation is followed by sulfitation.

The clarified juice is subjected to the same processes (multiple effect evaporation, concentration to a heavy syrup containing minute crystals in the vacuum pan, crystallization with stirring and temperature control, and removal of adhering liquids by the use of centrifugals and dryers) previously described under cane sugar.

The molasses from cane sugar contains so much invert sugar that recovery of sucrose by chemical means is not profitable. Beet sugar molasses contains very little invert sugar, but the sucrose content is around 50%. Further profitable crystallization is rendered impossible by the presence of 10% to 12% inorganic salts together with a variety of complex organic compounds, most of which contain nitrogen. The raffinose content of beet sugar molasses is from 1% to 3%. Sucrose has the property of combining with barium and strontium hydroxides to form insoluble compounds. Calcium oxide in finely divided condition is also used with sucrose solutions, but suspensions of calcium hydroxide are not satisfactory in their action. These substances are commonly represented as molecular compounds, as for example, $C_{12}H_{22}O_{11} \cdot 3CaO$, and are called "saccharates." Recent investigations indicate that they are not chemical compounds, but are colloidal in their nature. The higher saccharates are insoluble, and are more or less free from contaminating materials, the purity varying with the nature of the recovery process and the composition of the molasses. They decompose readily in the presence of carbonic acid to free sucrose and to give a precipitate of the corresponding alkaline earth carbonate.

Strontium hydroxide is somewhat expensive, and the strontium process is not used in this country and in only one large molasses plant in Germany. Barium monosaccharate, $C_{12}H_{22}O_{11} \cdot BaO$, is quite insoluble and also readily broken up by carbonic acid to sucrose and barium carbonate. The barium process yields saccharate of high purity, but it is difficult to convert barium carbonate to the oxide on a commercial scale. The temperature of the electric furnace is required to decompose barium carbonate directly. The recently developed Deguide process involves mixing barium carbonate with silica and heating in a rotary kiln. At this temperature the barium forms a disilicate, which decomposes to the monosilicate on leaching with water and yields half of the barium in the form of barium hydroxide. The residue is mixed with additional quantities of barium carbonate. This process is now

successfully operated in a large recovery plant in the United States which handles the molasses from a number of beet sugar factories. The method otherwise used in the United States is the calcium saccharate process. Calcium trisaccharate, $C_{12}H_{22}O_{11} \cdot 3CaO$, is practically insoluble in water, and by regulating temperatures and concentrations it is possible to produce the trisaccharate almost exclusively. The molasses is diluted with water to about 6.5% concentration of sucrose, and in some cases from 10% to 15% of the theoretical amount of calcium hydroxide is added as a suspension. The solution is then chilled to 10° C. and finely powdered quicklime in about double the theoretical amount is added with thorough stirring and cooling. The temperature is never allowed to rise above 20° C. About 93% of sucrose is removed as insoluble tricalcium saccharate, which is separated by filtration. The filtrate contains soluble saccharates, and on heating to boiling, tricalcium saccharate is formed and removed by continuous filters or thickeners. The saccharate cake instead of milk of lime is added to raw juice. Tricalcium saccharate undergoes some hydrolysis to give the necessary alkalinity, and on carbonation calcium carbonate and sucrose are formed. The prices of sugar and molasses determine whether or not it is profitable to recover sugar from beet molasses.

Sugar Refining. Most cane sugar, as produced in the mills previously described, must be subjected to a refining operation. If the refineries and sugar mills are operated together with the closest possible cooperation, certain economies are possible, but refineries are often located near large cities far away from the mills. The refining is essentially a problem of removal of coloring matter and other impurities from sugar solutions by means of adsorbing materials, and the recrystallization of sucrose. The quality of color is more important than the depth. Red colors due to excessive liming are specially objectionable and require large amounts of bone-black for removal, and the last traces of green coloring matter from polyphenols are very resistant to complete removal. The average sucrose content of the raw sugar that comes to a refinery is about 97° V. Polarization tests on a raw sugar are not an exact measure of sucrose content. There is considerable variation in the way sugars will behave in the refinery. Hence chemical analysis must be correlated with refinery experience.

The raw sugar is mixed with clear syrup and run in centrifugals. This serves to wash the crystals and materially improve their color, and to raise the sugar content to about 99% of solids. The molasses adhering to crystals of raw sugar contains not more than 65% sucrose.

The sugar from the first centrifugals is dissolved in water or in dilute sugar solutions to make a solution of 60% or more sugar content, which has considerable color. The syrup resulting from washing the raw sugar in centrifugals is put through the same process as the solution of washed sugar, and what is said about one is to be regarded as applying to the other. These solutions are pumped to the top of the refinery and placed in tanks called "blow-ups." There the solution is treated with the necessary amount of lime and an adsorbing material, this being in modern refineries mainly diatomaceous earth or "kieselguhr."

The contents of the blow-up tanks are filtered, usually by pressure leaf filters, and the filtrate is then run to pressure tanks and thence to large cisterns, filled with bone-black, which have capacities of 1200 to 2500 cu. ft. At the bottom of each is a grating supporting a coarse blanket to prevent the escape of "char." This material is made by heating coarsely ground bone in closed retorts. The organic materials decompose with the deposition of carbon, which makes the whole mass an intense black but which is not over 10% of the entire weight. The main component is calcium phosphate, and a little calcium oxide is present in freshly calcined material. Decolorizing carbons of vegetable origin have been used to a certain extent, but bone-black is still standard material in sugar refineries. The char is from 16 to 30 mesh. The passage of colored sugar solutions through char filters serves to produce a colorless liquid. Char that will not remove all the color from a solution may still be used on darker liquids, and it is not put out of service until it has reached the limit of its decolorizing ability. Spent char is washed free of sugar, drained, dried, and passed through vertical cast-iron retorts heated by burning producer gas. The adsorbed organic matter undergoes destructive distillation at temperatures of 1000° F. or higher and leaves in the char a small amount of carbon. The char passes through coolers, which are essentially air-cooled iron tubes, and thence to screens to remove fines. The screened char is then returned to the char filters. Replacement of char in a year of continuous service means only between 15% and 30% of the total amount in use. All solutions pass through a filter gallery, where samples are placed in racks over windows for color testing.

The colorless syrup is sufficiently concentrated to be handled by a vacuum pan, but all refineries are equipped with multiple effect evaporators to concentrate washings and all recovery solutions. Since the solution fed to the vacuum pan contains only traces of substances other than sucrose, it is easier to produce crystals of the desired size

and hardness than in the case of the raw sugar. The operations of evaporation, crystallization, and removal of liquid with spray washing in centrifugals are essentially the same as previously described. It is essential to remove adhering solutions as quickly as possible to prevent secondary grain formation. Moist sugar from the centrifugals may be formed into cubes or tablets and hardened by baking. The bulk of the product of the centrifugals is sent through rotary dryers heated by steam coils, which reduce the water from 2% to mere traces, usually from 0.01% to 0.02%. Thence the dried sugar goes to coolers built like the dryers, but with air supply cooled over water coils. The sugar crystals are screened and the fines are either remelted or reduced to a fine powder and sold as confectioner's sugar.

All washings are reworked, those that are dilute being concentrated in multiple effect evaporators before they are sent to char filters and "strike pans." These include the washings of the char filters, filter press, bag filters, and the bags in which raw sugar was shipped, and the syrups from the last centrifugals. The molasses from cane sugar refining is made into ethyl alcohol.

STARCH

Starch is a colloidal carbohydrate which corresponds to the empirical formula of $(C_6H_{10}O_5)_n$. Starch granules are of microscopic size and are usually spheroidal, their shape varying with their source. No chemical changes are involved in the production of starch. When a suspension of starch is heated in the presence of an acid, hydrolysis takes place. The first products are soluble polysaccharides of high molecular weight and great optical activity, which bear the general name of dextrin. The first crystalline substance that may be identified is maltose, $C_{12}H_{22}O_{11}$. This in turn hydrolyzes to dextrose, $C_6H_{12}O_6$. During most of the period of hydrolysis unchanged starch and all hydrolysis products are present.

Starch occurs in practically all plants. The chief commercial sources of starch in the United States are wheat, potatoes, and corn. Potato starch is made by reducing the raw tubers to a fine meal and washing out the lighter material from the heavier starch. Wheat starch is the result of a combination kneading and washing process in which the starch floats away in water while the gluten remains as a plastic mass. In foreign countries, large commercial quantities of starch are made from the manioc plant, which produces a tuber known as cassava root. From this is obtained cassava starch, popularly

known as tapioca starch. Starch in considerable quantities comes from the sago palm. Tapioca, sago, and arrowroot can be economically produced only in tropical countries. Most rice starch is produced in Japan, and practically none in the United States, owing to the high cost of producing rice. The most important source of starch in the United States is maize or Indian corn, known in this country simply as "corn." Commercial corn as received by starch plants has an average composition as follows.

	AS RECEIVED	DRY BASIS
Moisture. . .	15.8	
Protein. . . .	8 9	10 6
Fat.	3 9	4 6
Fiber. . .	2 4	2 8
Ash.	1 3	1.5
Carbohydrates.	67 7	80 5
	100 0	100 0

Corn is thoroughly cleaned and is then steeped at 50° C. for 36 to 48 hours in a 0.2% solution of sulfurous acid which passes counter current through a series of tubs. This treatment prevents bacterial growths and serves to soften the grain. About 5% of the weight of the corn is extracted, partly by enzymatic action and partly by simple solution. The steepwater is evaporated and the concentrated syrup so obtained is mixed with other by-products to be used as stock feed.

The soft grain is first disintegrated by attrition mills in which the material passes between rotating plates equipped with teeth. The tough germ is separated but is not broken up. The germs are floated in starch suspensions while heavier portions of the grain sink. This separation is accomplished by means of a spiral agitator at the bottom of a short deep trough and rakes at the top of the trough. The germs are freed of adhering starch by sifting and washing in reels, and after squeezing and drying they are sent to expeller mills for the production of corn oil.

After removal of the coarse hulls, the remainder of the grain is ground wet in buhrstone mills, and bran is removed from starch and gluten by cloth-covered shaking screens and reels. The amount of water is kept low, and the counter-current principle is employed. The bran is reground, washed, and screened several times to remove as

much starch as possible, and finally pressed, dried, and made a component of stock feed.

Starch is heavier than gluten, and may be settled out by flowing the suspension of the two through long shallow troughs known as "tables." These are ordinarily 120 ft. long and 2 ft. wide. A deep layer of starch accumulates at the upper end, and gradually becomes thinner until the last few feet are free from starch. The "tabling" operation is carried out several times. The starch is flushed from the tables each time with water into large tanks, where it is kept in suspension and returned to the tables. After the last tabling the starch is filtered in a press equipped for washing.

The crude gluten, still carrying considerable starch with it, is collected by allowing its suspension to settle, and the water is largely removed from it by filter presses. The crude gluten is made into a product known as "corn gluten meal" containing about 40% protein, which is used as a stock feed. Another product used for the same purpose is made up of a mixture of gluten, hulls, and the syrup resulting from the evaporation of the steepwater.

Starch Products. There are various grades of starch, their physical form depending on the way they are dried. The cake from the filter presses, placed in wire baskets and dried rapidly in tunnel dryers, forms "pearl starch." If the cake is subjected to hydraulic pressure and then very slowly dried, it breaks up into lumps commonly called "starch crystals." Pearl starch is run through beater mills and then carefully "bolted" in reels for the removal of hard, overdried particles and lumps of protein materials, the product being "powdered starch." Powdered starch may be steamed under high pressure, and the cake crushed and screened to the desired size, this material being "lump starch."

Starch dried without further treatment is "thick boiling starch." When heated with water it forms a thick paste which cools to a tough, firm jelly. If the starch is treated with acid to incipient hydrolysis and the acid immediately neutralized, the product, known as a "thin boiling starch," forms much less viscous suspensions. The term "soluble starch" is loosely used to describe a mixture of hydrolysis products made by the action of atomized acid on dry starch. When hydrolysis has gone so far as to destroy the structure of the starch granule, the product has the name "dextrin." It refers to a mixture of soluble and insoluble carbohydrates, the portion soluble in water varying from 20% to 99%. The water-soluble substances are practically tasteless and are optically active to a very high degree. Except

for that which is formed in the manufacture of corn syrup, all commercial dextrans are made dry, that is by the action of acid mists and vapors on dry starch. "Chlorinated starch," made by the action of chlorine, is of some importance.

What were once known as "British gums" were starch hydrolysis products, the change being brought about by heat and the moisture in the starch granules. At present there is no sharp distinction between dextrin and British gums, because products similar to the original gums are now made both with and without acid.

Starch is a widely used food, and the technical grades find use largely with textiles, both in the laundry and as a sizing in the weaving and finishing of cloth. An important use of dextrin is in making the pastes with dyes for printing of cloth. Dextrans and gums are very generally employed as adhesives, particularly with paper products.

Corn syrup or commercial "glucose" is made by carefully regulated hydrolysis of starch suspensions by means of dilute hydrochloric acid under pressure. The resulting product is a solution containing dextrin, maltose, and dextrose in varying proportions. Wet starch is made into a thin suspension and added slowly to hot, dilute hydrochloric acid in converters, which are essentially vertical cylinders of copper or resistant alloys of about 2200 gallons' capacity. After the converter is closed, pressure is brought up quickly by means of the introduction of steam. The time, the concentration of acid and starch, and the pressure all vary with the desired product, but a typical example involves the use of 22° Bé starch suspension, 2% hydrochloric acid, 30 lb. steam pressure, and a time of 22 minutes. If dextrose or corn sugar is to be made the values in the above example would be changed to 45 lb. pressure and 35 minutes' heating.

When the reaction has proceeded to the desired point, the liquid in the converter is discharged into a wooden tank and treated with sodium carbonate to neutralize the free acid, to precipitate organic colloids, and to remove any iron in solution. Filter aid is added and the solution is filtered, the filtrate being clear but highly colored. Color is removed by passing the liquid through char filters. Because of the presence of calcium hydroxide, which has a harmful effect on the syrup, the char must be treated with dilute hydrochloric acid and afterwards thoroughly washed with soft water to remove calcium chloride. Other than this "tempering" operation, the handling of char filtration and reburning of spent material is the same as in the refining of sucrose. Vegetable chars also find considerable use as decolorizing agents.

The thin syrup that is drawn from the char filters is sent to multiple effect evaporators and concentrated to a density of about 30° Bé, during which operation it acquires considerable color. This requires a second char filtration, after which it is concentrated in vacuum pans to the finally desired density, which is usually between 40° Bé and 50° Bé.

In addition to specific gravity, commercial glucose is designated by the term "percentage purity," which refers to the amount of reducing sugars present, and is a purely arbitrary method of evaluation. In glucose these are from 40% to 45%. Corn syrup that is used for technical and industrial purposes or that is intended for export may be treated with small amounts of sulfites to insure against development of color under prolonged storage conditions. Even in these cases the amount does not exceed 0.035% in terms of sodium bisulfite, which is the limit permitted in food products in the United States. Sulfites are not added to corn syrup used as a food product in the United States, either for the purpose of deodorizing or bleaching. Refining processes have been so perfected that sulfites are not necessary. Only a mere trace, not exceeding 30 parts per million, of sulfurous acid is carried over from the steeping process into the final product. Such corn syrup complies with all food law requirements regarding purity and freedom from sulfurous acid and sulfites. Glucose is used with sugar, flavors, and refiner's syrup in making table syrup. It is also used very largely in making jellies, jams, preserves, and in all sorts of pastry and confectionery, not only being wholesome and digestible, but also having the property of preventing crystallization of sugar.

CELLULOSE

The carbohydrate known as cellulose is the main component of plant fiber. It occurs in relatively pure form in the seed hairs of the cotton plant, but in most plant fibers it is associated with a variety of substances such as oils, waxes, tannins, pectin, and lignin. Cellulose corresponds to the formula $(C_6H_{10}O_5)_n$. The unit of which the cellulose molecule is made up is now regarded as four rings, each linked by oxygen atoms and each made up of five carbons and one oxygen, to each ring of which is attached a $-CH_2OH$ group. Cellulose is colloidal in its nature and does not form true solutions in any solvent. Recent work by colloid chemists based on the use of very powerful centrifuges indicates a probable molecular weight of between 35,000 and 45,000. Lengthwise orientation of colloidal particles is also indi-

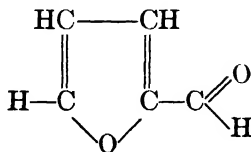
cated. Cellulose functions as if it contains three hydroxyl groups for every six carbons. Most commercial derivatives of cellulose, such as nitrates, acetates, and xanthogenates, depend for their formation on these hydroxyl groups.

Cellulose reacts with sodium hydroxide, probably forming unstable alcoholates. These are broken up by water, leaving a material that has the same empirical formula as cellulose, but with increased power to absorb water and dyes, greater chemical activity, and increased readiness to undergo hydrolysis. The treatment with alkali, and subsequent removal of the alkali with water, cause a swelling of cotton fiber.

Cellulose may be hydrolyzed under the influence of high hydrogen ion concentrations. Partial hydrolysis results in a material reducible to a powder, and known as "hydrocellulose," which has strong reducing properties. Complete hydrolysis produces dextrose in good yields.

Associated with cellulose in plant tissues are oils, fats, waxes, and tannins. In certain plants, such as flax, pectins are present in variable quantities. In wood and in the mature woody stems of straws, the cellulose is associated with many other substances, among which the most important is a complex substance known as lignin. Although the constitution of lignin is not known with certainty, it appears to have double bond linkages, methoxy groups, and carbonyl groups.

There are also substances in plant tissues known as "hemicelluloses," which are insoluble in water and quite variable in their solubility in both acids and alkalies, and which undergo hydrolysis more readily than cellulose. Those yielding hexoses on hydrolysis are called "hexosans," and those producing pentoses are "pentosans." The production of xylose from pentosans has already been described. When pentosans are digested under pressure in the presence of dilute acid, furfural is obtained in good yield. Furfural has the structural formula



Researches carried out some years ago in government laboratories indicated that furfural could be made from the pentosans of corn cobs, but the cost of collection of the raw material made the process unattractive. Large quantities of oat hulls were available as a by-product in the manufacture of rolled oats. These hulls were incorporated with

stock feeds as a roughage, and some work was done with a view towards converting a part of the cellulose of the hulls into sugar by means of acid. It was found that it was more feasible and profitable to digest with acid under pressure and make furfural from the pentosans, which are present in the hulls in an amount equal to that of cellulose.

The general procedure includes wetting the hulls with a 6% solution of sulfuric acid and passing steam through this mass in a rotary digester. Pressure is maintained at 60 lb. per square inch, and the furfural is removed continuously with the steam. Entrained solids are removed, and the steam passes into a copper fractionating column. The final product of the column is a crude furfural containing some 16% water. The water is removed by heating the crude product in an enclosed pan equipped with spiral baffles, the product of this process being technical furfural of 98% to 99% purity.

It has only been a few years since five pounds of furfural cost what a tank car of the material costs today. Among the uses of furfural are the following: fungicide, germicide, herbicide, solvent, and starting substance for numerous valuable derivatives including furan, furoic acid, furfuryl alcohol, hydrofuramide, and hydrogenated compounds. Furfural is used in the manufacture of synthetic resins, and is particularly valuable in light-sensitive resins used in etching. It is already occupying an important position in the lacquer industry. It is too early in the history of the industry to predict the ultimate position of furfural, but it has already become a very important industrial chemical.

I. Unchanged Cellulose Products

The main products made up very largely of unchanged cellulose in a fair degree of purity are cotton and linen fabrics and paper.

Cotton. Cotton fiber is a seed hair. When exposed to the air, the tubular filament dries to the form of a flat and slightly twisted ribbon. After being removed from the seed, the filament is from 0.75 to 1.5 in. long. The average of a large number of analyses of clean cotton fiber made by the United States Department of Agriculture shows the following.

Water	6.74%	Fiber (cellulose)	83.71%
Ash	1.65%	Nitrogen-free extract	5.79%
Protein	1.50%	Fat (or wax)	0.61%

Some of the analyses of unbleached cotton indicate a higher cellulose content, around 90%.

Wax is removed from cotton fiber by a saponification process in which dilute solutions containing hydroxyl ions from some source are used. If calcium hydroxide is used, it must be followed by dilute sulfuric acid and a second treatment with caustic soda (or sodium carbonate) and soap. The use of lime has largely given way to simple boiling with 1% to 2% caustic soda solution. Cotton cellulose is not injured by the action of such dilute alkali, but stronger solutions render it very sensitive to oxidation. The boiling is carried out in an apparatus known as a "kier" in which the material is held between perforated plates and the washing solution is circulated through it either at atmospheric or a somewhat higher pressure. The fiber may also be washed with soaps made by the action of sulfuric acid on glycerides, but this is regarded mainly as a softening operation. Bleaching is brought about by mild oxidizing agents, mainly hypochlorites. Hypochlorite ion breaks down slowly to chloride ion, freeing oxygen, which reacts with the coloring matter of the cotton fiber. Hydrogen peroxide is necessary where cotton-wool and cotton-silk mixtures are to be bleached. When a thorough bleaching of cotton is not required, hydrogen peroxide is added in an open kier in which boiling is taking place. This method of bleaching is said to be increasing. All bleaching operations tend to weaken cellulose fibers.

The making of yarn, thread, and fabric is entirely mechanical.

Linen. The fiber derived from the stalk of the flax plant is known as linen. If the plant matures and produces seed, its fiber is worthless in the production of textiles. The fiber must be freed from all other components of the stalk in an operation known as "retting." As yet no satisfactory chemical process of retting has been developed. The stalks are bound in bundles and steeped in soft, stagnant water. The process is one of fermentation.

Linen fiber is made up of a series of cells, each about the same size as a single cotton cell, which are cemented together by an intercellular material, mainly calcium pectate, the whole forming coarse filaments one to three feet long. Very great care must be exercised in preparing the fiber for final use, since it is necessary to remove wax and excess pectin bodies without attacking the material that binds the cells together. The treatment includes a series of boilings with dilute caustic soda solutions, followed by treatment with dilute acid and thorough washing with water. Linen is bleached in very much the same way as cotton. Hypochlorite is the most common bleaching agent used. Ozone may be allowed to act on the fiber, which has previously been dampened by ammonium hydroxide.

Paper. The earliest writings on a flexible material were on specially prepared sheepskin. The Egyptians substituted thin sheets of the papyrus plant, which were glued together and built up into layers and finally pressed into a homogeneous sheet, hence the derivation of the modern word "paper." The first material at all resembling modern paper was made by the Chinese from bamboo and rags, and the art was brought from China by the Arabs into Europe. In the earlier years of paper-making only rags were used.

A limited amount of paper, mainly the finest grade, is made from cotton and linen, but more than 75% of the writing papers are made entirely of chemical wood pulp (sulfite or soda). Much of the remaining 25% contains some sulfite pulp (so-called "rag content" papers). The bulk of paper is made from wood pulp, prepared by chemical treatment of wood. The cheaper grades of paper, such as newsprint and wall paper, contain mainly the crude fibers made by grinding wood. Other fibrous materials such as jute, hemp, straw, sugar-cane wastes, cornstalks, and waste flax may be made into paper, usually with a preparatory chemical treatment. A great deal of paper is used over again, either with or without removal of ink, being reduced mechanically to a suspension of individual fibers in water.

Rags of cotton and linen, and scraps and trimmings from garment factories, are freed from dust, shredded, and boiled under pressure in alkaline solutions in order to remove dirt and grease, and also any wool which may be present. They are afterwards washed and worked into individual fibers in a beater equipped with a special washing cylinder on the opposite side of the tub from the beater roll. As a result of these operations the rags lose 25% to 40% of their weight.

Waste paper may be partially or wholly freed from printer's ink by treatment with dilute caustic soda to saponify residual linseed oil, and washing in machines designed to give very rapid circulation of water, which serves to scour the fibers. Most waste paper finds its way into paper board, in the making of which office wastes, magazines, and newspapers are mainly used. No effort is made to remove ink from board stock, the paper being reduced to a smooth suspension of fibers by the use of beaters.

Mechanical wood pulp is made by holding short sections of logs, from which the bark has previously been removed, against rapidly moving grindstones over which water continually flows. The logs are held in position and forced against the stone by the platens of hydraulic presses, either individually or in a magazine. Mechanical wood pulp is a rich cream color. It may be bleached by sulfurous acid and

sulfites, but the color is most commonly compensated by the use of a blue dye. Screens of various sorts remove slivers, after which the fibers are used directly in the form of a suspension in the manufacture of newsprint. A comparatively small quantity is freed from water for shipment.

In order to use wood as a raw material for making paper of the grade and nature of book paper, it is necessary to subject it to some process of chemical treatment for the purpose of obtaining relatively pure cellulose. A less drastic chemical treatment of wood by the sulfate process results in a very strong but highly colored paper, generally known as "kraft" to indicate its toughness. White paper is made from approximately pure cellulose.

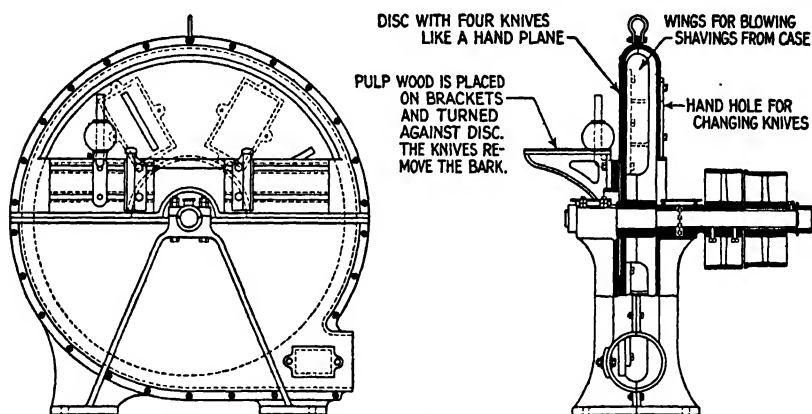


FIG. 108.—Barker. Courtesy Carthage Machine Company, Carthage, N. Y.

Before any chemical treatment can be applied, the wood must be reduced to chips. Most paper in the United States is made from spruce and poplar, but many other kinds of wood are used, both the hard woods and the coniferous woods. The logs are cut into short sections, and the bark is removed by tumbling the logs in huge cylinders made of steel bars spaced so as to prevent the escape of the logs, by rolling in pockets in which they are lifted and lowered by cams, and slicing off the bark by knives on revolving disks. A stream of water washes away the bark as it is rubbed off in the first two methods. The logs are then sliced into slabs about seven-eighths of an inch in thickness by being held at an angle against huge revolving disks, each disk weighing around three tons and carrying several heavy knives set like the blade of a wood plane. The slabs of wood are broken up into

chips by swinging blade or cage crushers, and are screened to get rid of dust and oversize chips.

1. *The Sulfite Process.* Digestion of wood chips under pressure in a solution of sulfurous acid and calcium acid sulfite, $\text{Ca}(\text{HSO}_3)_2$, is known as the sulfite process. The average cooking solution contains from 4% to 7% sulfur compounds in terms of sulfur dioxide, at least three-fourths of this being sulfurous acid and the remainder calcium acid sulfite. These reagents have very little effect on cellulose, but decompose lignin and hydrolyze polysaccharides. Dextrose is formed in this process and appears in the waste liquor, but because of reducing conditions no sugar acids are formed. Acid sulfites add to double bonds and to carbonyl groups. Calcium acid sulfite on heating decom-

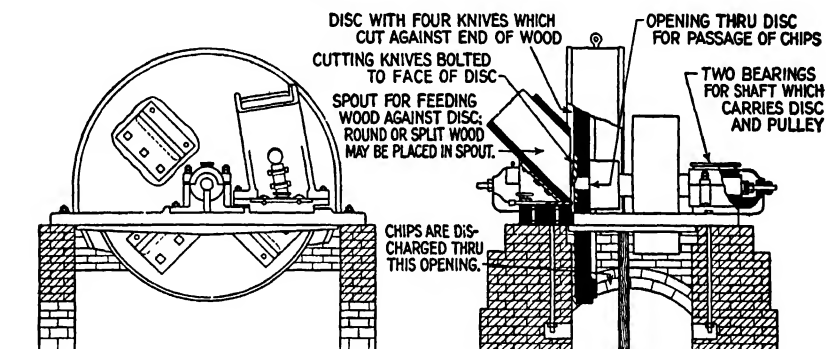


FIG. 109.—Chipper. Courtesy Carthage Machine Company, Carthage, N. Y.

poses into the neutral sulfite and sulfurous acid. The hydrogen ion concentration of the cooking solution must be relatively low, since hydrolysis of the cellulose must be avoided.

The digester acid is made by the action of sulfurous acid on a suspension of calcium hydroxide, or much more commonly by passing sulfur dioxide over wet limestone. Most sulfur dioxide is made by burning sulfur in pan, rotary, or spray burners, but some is made in pyrite burners. The limestone is packed in tall concrete towers lined with acid-proof brick, and water is run down over the stone. The sulfur dioxide, after cooling, is passed up the tower. From two to four towers are used in series. The liquid that is drawn from the base of the tower first receiving the gas is run down towers filled with some sort of packing material, and waste gases from the digester pass up these scrubbing towers. Any sulfur dioxide that escapes from the recovery tower is not lost, since the gases from this tower are mixed with the gases from the burners.

A digester is a cylindrical shell with a dome-shaped top and a conical bottom, made of sheet steel in riveted sections, and lined with acid-proof brick bonded with acid-proof cement. Between the lining and the steel shell of the digester there is a layer of portland cement-sand mortar. A typical digester will hold about 27 cords of wood, and has the outer dimensions of 15 ft. in diameter and 49 ft. in height. The most common method of heating is to admit steam directly to the digester. There is a definite trend towards the use of forced circulation in sulfite digesters for the sake of greater uniformity of cooking conditions and a more uniform product. The temperatures vary dur-

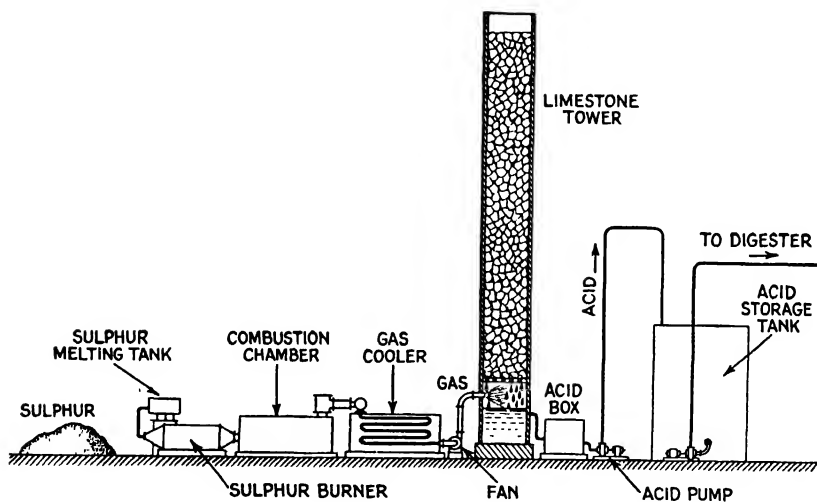


FIG. 110.—Sulfite Process Acid System. Courtesy Hammermill Paper Company, Erie, Pa.

ing a run from 110° C. at the beginning to 145° C. at the end, and pressures are of the order of 65 to 70 lb. per square inch. Excess gases are removed in order to maintain a constant pressure, and from them liquids are condensed and the gases are sent to the recovery system. The time of digestion varies from 7 to 60 hours, but rarely runs over 20 hours.

At the end of the operation the valve in the bottom of the digester is opened, and the gas and steam pressure drives the cooked chips into covered tanks of wood or concrete. The impact against an iron plate or the concrete wall breaks up the soft bundles of fiber that were once chips into individual fibers. The liquid is drawn from beneath perforated plates or tile in the bottom of the tanks. It may be evaporated

to a pitch and used as a binder for briquetting powdered coal. It contains fermentable carbohydrates from which industrial ethyl alcohol is made to a limited extent. Resinous woods yield considerable quantities of such liquids as cymene, valuable as a solvent and in synthesis of organic compounds. For the most part, however, recovery of sulfite waste liquor is merely a matter of avoiding the nuisance of stream pollution.

The pulp from this process is washed free from acids and is put through an elaborate screening and settling process for the removal of

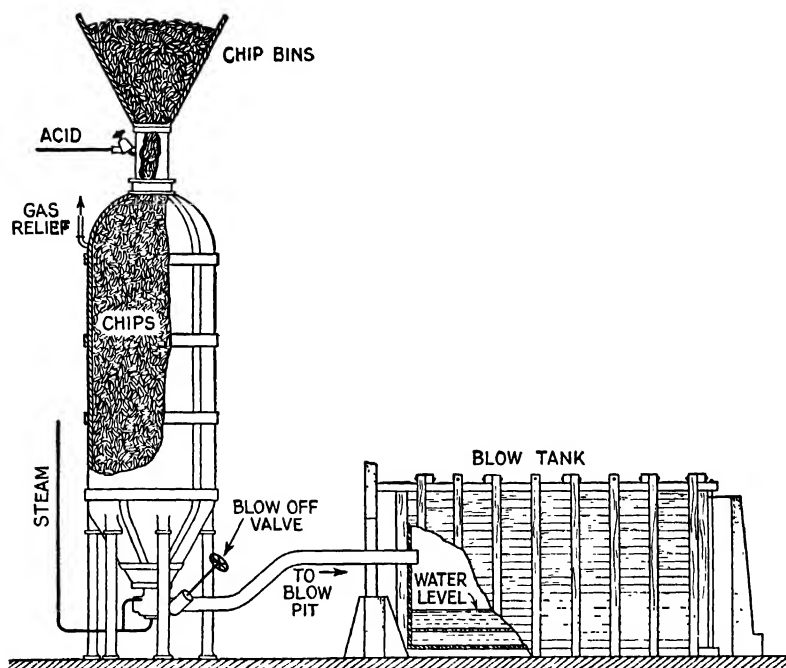


FIG. 111.—Sulfite Digester. Courtesy Hammermill Paper Company, Erie, Pa.

oversize particles, uncooked chips, and grit. The pulp is freed from most of its water by drums of reinforced wire screen with closed ends which are partially immersed in tanks containing a fairly thick suspension of the fiber. Water runs through the screen and, as a drum revolves, a thin layer of pulp adheres to its surface. This may be lifted off by a rubber roll and scraped from it to storage, or it may be removed by press rolls and squeezed into a sheet, which is cut into sections that are folded and pressed to form the “laps” that are sent to the paper mill. In recent years, modern continuous filters are being

used not only in the recovery of fiber from washings and paper machines, but also in washing and as substitutes for the "deckers" just described. The screenings are ground to recover additional fiber.

Color is removed from pulp by hypochlorites derived either from bleaching powder or more commonly from the action of chlorine on a suspension of calcium hydroxide. If bleaching is carried to a "high white" color, there is likely to be some oxidation of the cellulose with resulting damage to the fiber. It is better to leave a little color in the fiber, and compensate it by a blue dye. Various types of equipment are used in bleaching paper pulp, including beaters, rotating shells, tanks and tubs of all sorts, equipped for stirring and circulation. The operation requires several hours and consumes a large quantity of power.

2. The Soda Process. The soda process involves the digestion of wood chips under pressure with a dilute solution of sodium hydroxide. The woody tissues are broken up with the formation of soluble compounds, and about half of the weight of the wood is left in the form of practically pure cellulose fiber. The caustic soda solution is usually from 7% to 8% concentration for ordinary air-dry wood, but may be higher to compensate for additional moisture. It is estimated that the weight of the sodium hydroxide should be about 25% that of the wood. The digesters are very much like those used in the direct sulfite process, but are unlined and smaller. They are usually heated and stirred by steam, but circulation may be aided by the use of a pump, and liquid may be withdrawn and heated outside the digester in high-pressure steam heaters. Some rotary digesters are also used. The pressure runs from 100 to 130 lb. per square inch. Progress has been made in the recovery of turpentine and rosin from pine wood in connection with the use of the soda process. When treatment has reached the desired point, the contents of the digester are discharged tangentially into a separator tank. In some mills the escaping steam is condensed in water, and the hot water is used in washing the pulp. The material in the tank is a suspension of fiber in a solution containing free caustic soda and organic compounds, very largely sodium salts of organic acids. The liquid, called "black liquor," which is drained from the fiber, is a rose color but quickly changes to a dark brown. The fiber is thoroughly washed, but it has a grayish tint which is only removed by bleaching.

The "black liquor" is first concentrated in multiple effect evaporators from a density of 12–15° Bé to 30–40° Bé and is then sent to disk evaporators. By running to a still higher concentration in mul-

multiple effect evaporators, it is possible to omit disk evaporators entirely. The concentrated liquid contains enough organic matter to support combustion, but the efficiency is too low to depend on this organic matter alone. It is fed to rotary calcining furnaces fired with shavings and wastes supplemented by coal. The burning of the organic sodium salts in the presence of excess sodium hydroxide results in the formation of sodium carbonate. In the older plants some free carbon also forms, but modern recovery systems burn out all the carbon and recover the heat in waste heat boilers. The ash discharged from the calcining furnaces is either leached for recovery of sodium carbonate or is causticized directly with calcium hydroxide. Continuous agitators and thickeners are taking the place of batch causticization. Losses are compensated by sodium carbonate or strong caustic soda solutions from electrolytic chlorine plants.

3. The Sulfate Process. The sulfate process gets its name from the raw make-up material used, which is sodium sulfate. Niter cake is also used. The sulfate is added to the solids from the recovery process and reduced by carbon to sodium sulfide. The cooking liquor is a solution containing from 4% to 6% sodium hydroxide, and from 1.5% to 4.0% sodium sulfide, together with small amounts of sodium carbonate and sodium sulfate. This process is widely used where only partial purification of the cellulose is desired, although it is capable of producing an easily bleached stock of much the same nature as that from the other processes. Sodium sulfide has little effect in itself, since it hydrolyzes in the digester to sodium hydroxide and sodium hydrosulfide, NaSH , which functions somewhat like the hydroxide but less vigorously. The digestion is carried on in much the same way as in the soda process, but the time is usually much shorter, rarely ever going over 6 hours, and averaging $3\frac{1}{2}$ hours. Pressures are about 100 lb. per square inch. One of the great drawbacks of the process, which restricts its use to isolated districts, is the offensive odor of the gases escaping from the digesters and separating tanks. These contain methyl mercaptan, CH_3SH , and dimethyl sulfide, $(\text{CH}_3)_2\text{S}$. Considerable progress has been made in disposal of the waste gases through condensers and in burning the non-condensable material in the furnaces. The pulp is handled as in other processes, but requires a more thorough washing.

The recovery of the liquor drawn from the pulp in the sulfate process involves evaporation in multiple effect evaporators, pressure evaporators, heaters, and flash tanks, and calcination in somewhat the same way that the black liquor from the soda process is handled. The

ash from the rotary furnace is mixed with sufficient sodium sulfate to make up for losses, some sawdust often being included, and the mixture is heated in a smelting furnace, the heat from this furnace being used in the rotary calcining furnace. The calcination and smelting processes are also carried out as a single operation, the concentrated liquor being sprayed into a furnace equipped with dust chamber and waste heat boiler. An air blast at the bottom of the furnace keeps the carbon incandescent, and through it the fused chemicals discharge. Most of the sodium sulfate is reduced to sodium sulfide by carbon. The sodium salts originally present in the liquor appear as sodium carbonate. The fused alkali is dissolved and treated with calcium hydroxide to convert sodium carbonate to sodium hydroxide. The product of the causticizing unit is sent to the digesters. It may be diluted with the black liquor from the separating tanks if color is not objectionable.

Making Paper from Pulp. Paper refers to a sheet of felted fibers, made by a process in which agitation is combined with removal of water from a suspension of fiber. The making of paper is primarily a mechanical operation, but in making all papers on which writing and printing are done the fibers are made to take up by adsorption various substances which prevent the spreading of writing ink and improve the surface for use in printing. The finished sheet may also be coated with substances which give the desired appearance to the surface.

It is quite often the case that the pulp is made at mills located near where the wood grows, and transported to paper-making plants located near the point of distribution.

The first machine to which a suspension of fiber is fed is commonly known as the "beater," but is sometimes called the "Hollander." It consists of an oval tub in the middle of which is a partition running the long way, reaching to within about three feet of each end, and known as the "midfeather." On one side of the midfeather is a heavy horizontal cylinder or "roll" equipped with a number of sharp-edged bars or knives set parallel to its axis. Beneath this is a curved plate also equipped with knives set at a slight angle from those on the roll. The bed plate is continued in the form of a curved plate, backed with wood and known as the "back fall." Most of the roll side of the tub is covered. The space between the knives of the bed plate and the roll is quite small, but the clearance is very carefully regulated by adjusting screws. The tub is filled to within a few inches of the top with a suspension of fiber. As the roll revolves it draws the suspension through the space between the two sets of knives. The action of the beater has been aptly described as that of "cutting, bruising,

fraying, brooming, and splitting of the fibers." Unless the roll is sharply lowered, cutting does not take place to a great extent. The object of this operation is to give the fibers a form that makes felting into a sheet take place more readily. The circulation is reasonably rapid, and the fibers pass repeatedly under the knives.

Most of the material necessary for giving various papers certain desired properties is put in the beater tub. When writing ink is applied to paper made solely of fiber it tends to spread. Printing papers

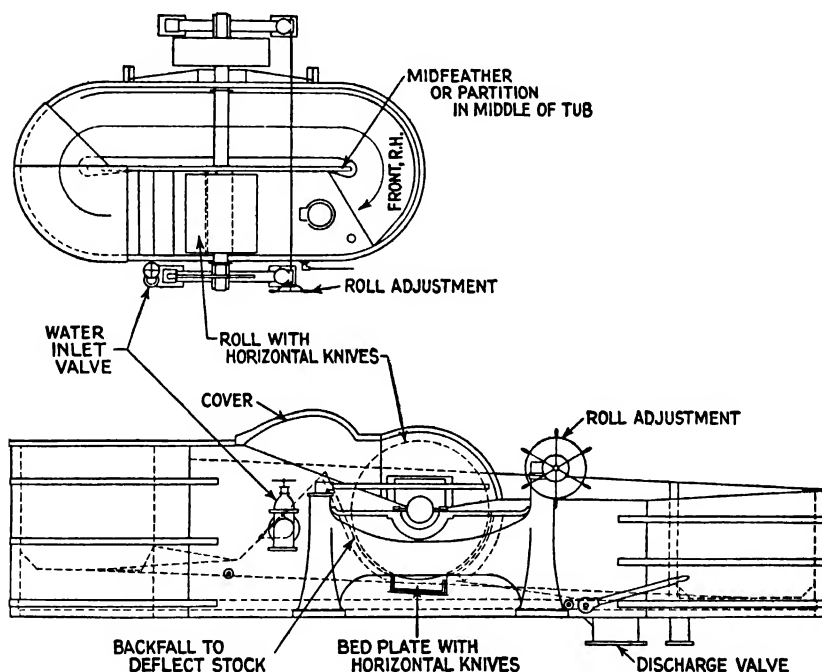


FIG. 112.—Beater or Hollander. Courtesy E. D. Jones and Sons, Pittsfield, Mass.

must have a surface that is so firm and smooth that loose fibers are not picked up by the type and cuts. Color is best fixed on the fiber at this point. A beater thus acts as a mixer, so that the sizing, loading, and coloring materials are properly dispersed. .

The spreading of writing ink is prevented by coating each fiber with "size." Sizing materials used in the beater result from mixing a solution of aluminum sulfate and "rosin soap." Just what is adsorbed by the fiber is not definitely known. It may be an aluminum rosin soap or it may be colloidal rosin and hydrolysis products including basic

sulfates and aluminum hydroxide. The quantity of alum used is not only more than is regarded as necessary to cause coagulation, but also more than is needed to make aluminum resinate. The sodium resinate is made by adding powdered pine rosin to a boiling solution of sodium hydroxide or sodium carbonate. After the sodium resinate a solution of aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, is added to the beater. This material is known as "paper-maker's alum."

Various "loading" materials are used in making paper, the most common of these being the finer grades of white clay, talc, pearl filler (anhydrous calcium sulfate), and "crown filler" (calcium sulfate dihydrate).

Paper is often colored by dyeing the fibers before they are made into the felted sheet, but in the making of some grades of paper, coloring is done later. Dyes are added to the stock in the beater after loading materials have been put in and usually after the sizing materials have been taken up by the fiber. The size is particularly valuable in the application of a dye, acting much in the same way as a mordant in textile dyeing. Some dyes are used in making white paper to offset complementary colors in the fiber. For some papers a blue-white color is obtained by the addition of a blue dye to the stock. White is regarded by the maker of paper as being as much of a color as red or green, and is obtained in much the same fashion.

From the beater, the suspension of fiber goes to the "Jordan engine," which consists of a conical shell lined with knives in which a heavy conical casting equipped with knives revolves at a speed of 300 to 325 r.p.m. The clearance between the two is quite small and is adjustable. The knives give a sidewise shear. The stock is fed into the small end of the machine and escapes at the upper part of the opposite end and is not returned. The main purpose of the treatment of the stock in the Jordan engine is a rapid cutting of the fibers into shorter lengths.

The stock is once more subjected to a careful screening operation to get rid of any materials not firmly held by the fiber. This operation includes the use of riffles, diaphragm screens, and rotary screens. The pulp is now ready for the actual making of paper. Practically all paper machines resemble each other very closely at what is known as the "dry end" from which finished paper comes. The differences are mainly at the "wet end," which receives the suspension of fiber in water. There are two main types of machines, those which make paper in the form of thin sheets which may be rolled and folded easily, and those which make relatively stiff sheets known as "board." It is nec-

essary to explain how paper is made "by hand" so that the general principle of paper-making may be understood. A screen of fine wire is fitted with a removable frame to form a shallow tray. This tray is dipped into a thin suspension of fiber. The openings are so small in the screen that the water runs out very slowly, being further hindered by the fiber that accumulates on the screen surface. If the contents of the tray are shaken skillfully, it is possible to cause the fibers to interweave in such a way as to form a sheet. When most of the water has drained through the screen, the frame or "deckle" is lifted and the screen turned upside down on a woolen blanket. The sheet of wet

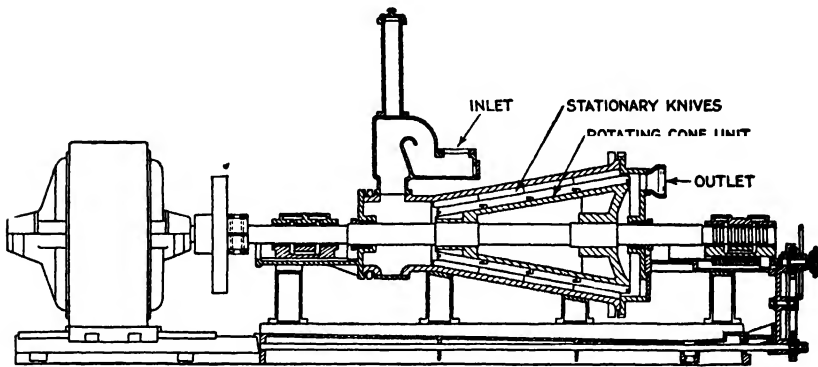


FIG. 113.—Jordan Engine. Courtesy E. D. Jones and Sons, Pittsfield, Mass.

paper adheres sufficiently to the blanket so that it may be peeled from the screen.

The machine on which most paper is made is called the "Fourdrinier." It consists essentially of four sections: a long tray which is shaken and whose bottom is a wire screen running as a belt; a series of rolls which squeeze and partly dry a continuous sheet of felted fiber; a series of steam-heated drums over which the paper passes; and a series of heavy, superimposed rolls, which give the final finish to the surface of the paper.

The first section of the machine accomplishes continuously what the hand-making method does intermittently: The suspension of fiber in water passes from the final screens into a reservoir known as a "head box" equipped with baffle plates and arranged to overflow at a definite and uniform rate. This overflow runs across a flexible apron onto the wire of the paper machine. The speed of the flow and quantity of water are regulated by two metal strips known as "slices,"

which are an inch or less above the wire at a point close to where the suspension is fed. The "wire" of the paper machine is a broad and rapidly moving belt of fine brass wire screen. Some paper machines will make a continuous sheet of paper 200 in. wide, hence this belt must be somewhat wider than this, that is approximately 17 ft. Most machines operate at speeds of 600 ft. per minute or less. The belt runs between two pulleys or rolls, each about 2 ft. in diameter, and is kept fairly taut. The roll near the feed end is called the "breast roll." The one at the discharge end is the lower "couch roll," and it may be equipped with a suction box. To prevent the stock from running off

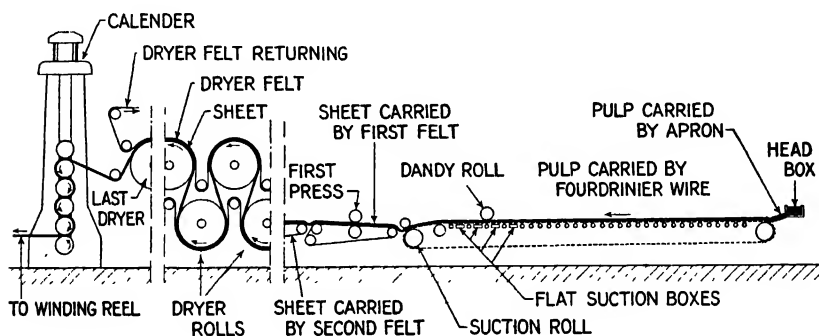


FIG. 114.—Diagrammatic Sketch of Fourdrinier Paper Machine.

the belt there are at each side rubber belts of square cross section called "deckle straps." These travel with the wire for about 10 ft. and are then returned overhead on pulleys. By this time the stock will not spread of itself. Beneath the upper surface of the belt is a series of small-diameter rolls of brass-coated steel tubing, which make contact with the belt, are turned by it, and serve by capillarity to draw water from the felted fibers. They are known as "table rolls." Beyond the rolls are a series of troughs with perforated wooden tops, against which the moving screen rubs. These boxes are equipped with suction devices so that water is forced out of the mat of fibers by atmospheric pressure. The wire, rolls, and suction boxes are held in a frame which continually vibrates with a sidewise motion. The fibers are given a forward movement by the rapidly running screen and are thrown back and forth at right angles to this direction, thus becoming thoroughly matted and tangled so as to make a sheet that is relatively tough when dry. The general orientation of the fibers is in the direction of the travel of the machine, so that there is marked difference in longitudinal

and sidewise shearing strength of the paper. As the paper moves forward it runs under a roll of screen wire, called the "dandy roll," which presses lightly on the wet paper and serves to smooth it. If the dandy roll is plain, the paper will be uniform in texture; but if it bears a design, that design will appear in the paper as the "water mark." In most paper machines a heavy, felt-covered roll, known as the upper couch roll, presses upon the sheet of paper just as it is ready to leave the wire, which is bending over the lower couch roll to reverse its direction. If the lower couch roll has within it a suction box, the upper couch roll is omitted.

The sheet of wet paper is carried over a short gap to the next section of the machine. This means perfect synchronization of speed, for the slightest difference would either tear the paper or cause an accumulation. The sheet passes between a series of rolls, which serve to squeeze water from it. A belt of woolen felt carries the paper as it moves between these rolls. The upper rolls are of wood or polished stone, and the lower ones are of iron covered with soft rubber.

The third section of the machine is used to dry the paper, which is made up of 65% or more of water. The dryers are a series of steam-heated cylinders, usually about 4 ft. in diameter. They are generally arranged in two horizontal rows so that the axis of a cylinder in the upper row coincides with the space between two cylinders in the lower row. A belt of canvas presses the continuous sheet of paper closely against the rolls, and by means of small auxiliary rolls causes the sheet to go as nearly as possible around each roll before it leaves it. By the time the paper has passed over all the dryer rolls, which often number as many as 32, it has reached a condition of sufficient dryness so that its moisture content will not change appreciably in contact with air of average humidity. The cloth, or "felt," has become quite damp and is returned over a series of drying cylinders before it again picks up the paper from the press rolls.

The last step necessary is a finishing operation which is carried out in a stack of heavy steel rolls called a "calender." The bottom roll of the series is positively driven at a speed corresponding to that of the rest of the machine. The other rolls are driven by friction, the first one with the bottom roll, each succeeding one by the roll below it. The paper passes from the dryers through a gap of several feet to the upper part of the calender, and works its way downward, being taken off near the bottom by reels. The rolls are equipped with scraping blades to remove any adhering fiber, and to prevent the paper winding up on them in case of a break, and are cooled by air blown

on them. The paper is rewound from the reels and cut into several rolls or made up in flat packages.

Paper board is made on cylinder machines. The wet end of such a machine is a series of tanks, each supplied with stock into which dip cylinders closed at each end, and with surfaces of fine brass wire screen, heavily reinforced and stretched on a framework of parallel bars attached to spokes from a central shaft. Water runs through the surface of each cylinder and is drawn off from the interior, while a thin film of fiber adheres to the moving surface. Felting takes place by virtue of vigorous agitation of the stock in each tank. A common felt passes above the cylinders and picks up one layer after another of fibers until a sheet of sufficient thickness is made. The press rolls are essentially the same as those of the Fourdrinier, but the dryers are operated without the cloth belt, since the sheet is thick enough to stand considerable strain. If colored cardboard is to be made, the first or first and last tank have stock the desired color.

A high gloss may be obtained by using the "supercalender," in which alternate rolls are of compressed fiber and steel; the rolls are allowed to become and remain warm by friction, the heat aiding in the polishing effect.

Paper or board from the machines is often coated in various ways. Coating materials include gelatin (glue), casein, starch and modified starches, "satin white" (a mixture of alumina and calcium sulfate), and "blanc fixe" (precipitated barium sulfate). One method of applying a coating is to spread the necessary material in the form of a paste on the paper surface by means of reciprocating brushes, to smooth it by rolls, and to dry it by means of festoon dryers. What is known as "tub sizing" is quite common at the present time in response to a demand for a hard-surfaced sheet, resistant to mechanical erasure. This is accomplished by dividing the drying rolls into two sections and using more dryers. The nearly dry sheet is either run through a tub containing the size solution or is sprayed on both sides with the solution, and is then dried again on the second section of drying rolls.

An interesting development in the utilization of wood, and one which promises to be of great value, involves the heating of wood chips with steam under very high pressure and bringing about disintegration by sudden release of the pressure. These are charged into very strong vessels known as "guns," and steam pressures of 200 lb. are maintained for 10 to 15 seconds, followed by 1000 lb. pressure for 3 to 5 seconds. A hydraulic discharge valve releases the pressure, and the contents of the gun escape at a velocity of 4000 ft. per second to cyclone sepa-

rators. The fiber is dropped into a "stock chest," refined as in the paper industry, and made into sheets 2 in. in thickness on cylinder paper machines. The sheet is rolled to a thickness of $\frac{3}{4}$ in., and is then put into hydraulic presses. Insulating board is reduced to $\frac{7}{16}$ in., and "pressed wood" to $\frac{1}{8}$ in. The latter product has all the qualities of the finest wood, and in addition has equal strength in all directions. It can be given the appearance of natural grain by a photographic process, and can be made to imitate very closely the most rare and expensive woods. This process is also regarded as having promise in the production of paper pulp.

Some progress has been made in the production of insulating board and pressed board from cornstalks, the process being an alkali digestion and the regular paper-making operation. The problem is largely an economic one, involving gathering and transporting the bulky raw material.

II. Cellulose Esters

The common esters of cellulose include nitrates, acetates, and xanthogenates. There are also a number of products obtained by the action of such reagents as ammoniacal copper compounds, concentrated sulfuric acid, and zinc chloride, which are not esters, but whose formation depends on chemical changes in the cellulose molecule.

Cellulose Nitrate. Cellulose nitrates, incorrectly called nitrocellulose, are not simple substances any more than cellulose itself is a simple substance. Theoretically the nitrate that contains the largest amount of nitrogen should have the formula $(C_6H_7O_2(NO_3)_3)_n$ or $(C_6H_7O_{11}N_3)_n$ with 14.1% nitrogen. In practice, however, the upper limit of nitrogen content is about 13.4%. The properties of nitric acid esters of cellulose vary with the percentage of nitrogen, all products being mixtures of a number of individual substances. As an illustration, the property of solubility in 1 : 2 alcohol-ether mixtures may be chosen, the solubility being measured as the fraction that will dissolve in an excess of solvent. Nitrates of 13% nitrogen content or higher are practically insoluble in this solvent. When the amount is 12.8% the solubility may be anywhere from 15% to 95% of the material. Below 12.7% the product is completely soluble in alcohol-ether until a value is reached which is the lower limit of commercially valuable material. The composition of the nitrate formed is a function of the composition of the mixed acid as well as of the time and temperature of nitration. The common varieties of cellulose nitrate of commercial use are as follows:

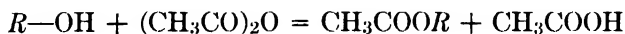
NAME	AVERAGE PERCENTAGE OF NITROGEN
Military gun-cotton (M. G. C.)*.....	13.2 to 13.4
Pyro	12.6
Soluble cotton	12.0
Pyroxylin	11.0

* Although it has recently been found possible to manufacture material with a nitrogen content of 13.4%, this is used only in propellant powders, and is not employed as a gun-cotton for torpedo heads. Most military guncotton manufactured as high explosive will be found to have a nitrogen content lying between 13.2% and 13.35%.

The raw material from which cellulose nitrates are made is for the most part cotton linters, or short-fiber cotton. The cotton is carefully purified by means of dilute alkali digestion, is reduced to a fluffy mass by toothed rolls, and is dried, usually in a continuous dryer. Iron pots are charged with mixed acid, and cotton is introduced through lids in the pot covers. Paddles immediately submerge the cotton and bring about thorough stirring. After nitration is complete, which requires only a few minutes, the contents of the pot drop into a moving centrifugal. Since most danger of fire is at this point, the time of handling and of acid removal by centrifugal force is reduced to a minimum. The contents of the centrifugal are dropped into tanks or immersion basins, and submerged by jets of water.

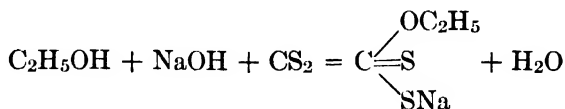
Cellulose nitrate may be purified by washing, pulping, and boiling in water and in dilute sodium carbonate, a process called "poaching." A very complete purification is necessary in making military propellants, but ordinary washing with water is sufficient for most cellulose nitrate products. Pulping is accomplished by such equipment as beaters and Jordan engines. Boiling with water and dilute sodium carbonate serves to break up sulfuric acid esters and to remove the free acid. All cellulose nitrates burn readily, and those with higher nitrogen content, when burned in a closed space, function as explosives.

Cellulose Acetate. Acetic anhydride reacts with hydroxyl groups of alcohols to form acetic acid esters.



Since cellulose contains alcohol groups, it functions in the same way to give a series of acetates. The cellulose must be carefully purified, and the production of acetate is accomplished by a mixture of acetic anhydride, acetic acid, and sulfuric acid. The resulting product will burn, but very slowly.

Cellulose Xanthogenate. When ethyl alcohol in alkaline solution reacts with carbon bisulfide, there is formed an alkali salt of xanthogenic acid, which is a sulfothiocarbonic acid ester.



The same type of reaction takes place between alkali cellulose and carbon bisulfide. If cellulose is treated with sodium hydroxide solution, it merely swells but does not lose its fibrous structure. If carbon bisulfide is brought in contact with this material, which has previously been pressed free of liquid, the xanthogenate is formed and dissolves in dilute caustic soda solutions. Further changes are allowed to take place by storing such solutions for a considerable length of time, the cellulose compounds losing a part of the sulfur originally present.

Cellulose Solvents. Metal ammonia compounds, the most notable of which is copper ammonia hydroxide, $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$, will dissolve cellulose, and a material of the same empirical formula as cellulose and free from nitrogen and copper compounds may be recovered from such solutions. Concentrated zinc chloride solutions containing hydrochloric acid will convert cellulose to a gelatinous mass which ultimately dissolves in the reagent. Sulfuric acid acting for a very short time causes the fibers of cellulose to become a homogeneous jelly, but if allowed to remain in contact with cellulose for any length of time causes complete solution, often accompanied by the deposition of free carbon.

Products of Cellulose Esters and Solutions. In most products in which the cellulose has undergone chemical change the cellulose fiber has disappeared entirely. In a few cases, only the surface of the fiber has undergone change. It is thus possible to get the cellulosic substance into some form other than a collection of short, individual fibers. The more important industries using products in which the original cellulose has undergone chemical change are those making explosives, textiles, lacquers, plastics, and coated fabrics.

Cellulose Nitrate Explosives. Most explosives are nitrogen compounds of some sort in which nitrogen has its highest positive valence. Black powder is a mixture of sulfur, potassium nitrate, and charcoal. Its place as a propellant in cannon and small arms has largely been taken by a cellulose nitrate product known as "smokeless powder." The cellulose nitrate used may be of the type soluble in a 2 : 1 ether-

alcohol mixture with a nitrogen content in the neighborhood of 12.6%, or it may be a mixture of the soluble type with a material containing in excess of 13% nitrogen. The first type of cellulose nitrate is used in the "pyro" cannon powder of the United States Government. The cellulose nitrate of higher nitrogen percentage is referred to as "insoluble nitrocellulose" because of its low solubility in ether-alcohol mixtures. When used in propellant powders, cellulose nitrate is thoroughly stabilized by giving it a prolonged boiling treatment.

The cellulose nitrate must be subjected to the very thorough washing, beating, and "poaching" process previously described. The suspended fibers are screened through brass plates equipped with fine slits. Centrifugals remove most of the water, leaving the cellulose nitrate with about 30% moisture. It is a very unsafe procedure to dry this material in the air, since more than 15% water is necessary to prevent ignition. Water is removed by the use of 95% denatured alcohol, since alcohol is to be used along with ether later in the process. The cotton is subjected to pressures of around half a ton per square inch in hydraulic pressures, and alcohol is pumped through the mass. The dilute alcohol that flows from the press is concentrated to 95% for the drying process or for making ether. The alcohol that remains in the block of cellulose nitrate is about 90% strength by volume.

The block of cellulose nitrate from the dehydrating operation is broken up in a revolving iron drum equipped with prongs. This material, which already contains all necessary alcohol, is charged into a closed mixer equipped with water jacket, and to it ether is added. All smokeless powder requires a "stabilizer." If oxides of nitrogen liberated in traces by decomposition of the cellulose nitrates were not removed, they would serve as catalysts to cause further decomposition. The heat developed would further increase the speed of reaction until fire or explosion would result. Diphenylamine is the most common stabilizer. It takes up nitrogen oxides, forming first a nitroso derivative, and then nitro compounds, until a nitrosotrinitrodiphenylamine is formed. The amount required to give ample protection is usually about 0.5% but is sometimes as high as 1.0% of the weight of the cellulose nitrate.

The product of the mixer resembles damp sawdust in appearance. It is first compressed at about one ton pressure to a dense block. This is then forced through a brass screen in a press called a "macaroni press," which operates at around 5000 lb. per square inch pressure. The threads are again compressed into a block. The material is now a dense, elastic, dark brown, colloidal jelly. Grains of powder are

formed by forcing the plastic mass through a die, and cutting the thread or rod into correct lengths. Small size powder consists of tiny cubes of colloidal cellulose nitrate, and most cannon powder is made up of cylinders whose length is about twice their diameter, and through which there are seven symmetrically placed parallel holes running the length of the cylinder. The whole object in shaping the grain is to produce a material that will give an increasing speed of burning and thus an increasing rate of gas production.

The powder is freed of as much solvent as necessary by circulating warm air through it. Final removal of the undesirable excess of solvent is accomplished by passing warm air through the powder contained in bins, or by circulating water through it, afterwards drying in air. The powder is then allowed to take up a certain amount of moisture, so that it will remain in equilibrium with air of average humidity. Powders for small arms are lightly coated with graphite to reduce danger of ignition by static electricity generated by the rubbing of the grains. Powders from the same process and same size of die differ slightly in grain size because of uneven shrinkage. In order to obtain a large lot of powder of uniform ballistics, 50,000 to 100,000 lb. of powder are taken from the dryer and blended by pouring them through hoppers into bins. During this operation moisture is sometimes added to bring the moisture content of the blend to the desired amount.

In some European countries and particularly in Great Britain nitroglycerin is used instead of alcohol-ether as a gelatinizing agent, a very powerful explosive being obtained but one which is said to cause excessive temperatures and considerable erosion. The British "cordite" is a propellant of this type. A powder known as "ballistite," formerly used in this country in shotgun shell, contained guncotton and from 40% to 50% nitroglycerin.

Cellulose Ester Plastics. The term "plastic" is broadly used to describe a material which is sufficiently soft to be given a desired shape, and which will retain that shape until it has hardened. The cellulose ester most widely used in the production of plastics is cellulose nitrate. Cellulose acetate is increasing in importance with lowering costs of acetic anhydride. Cellulose nitrate together with camphor and other ingredients may be gotten into the plastic condition by the use of solvents and very thorough mixing, this material being known as "celluloid." Millions of pounds of cellulose nitrate are used each year in making articles that have the appearance of ivory, tortoise shell, amber, and fine woods. The nitrate is lower in nitrogen content

than that used in making explosives, and burns less readily and much less rapidly.

Photographic Film. The substitution of a flexible, transparent celluloid film for a glass plate, and the rise of the motion picture to an industry of the first magnitude, have created an enormous demand for photographic film. Most film is made of cellulose nitrate. This is dissolved in organic solvents such as acetic acid esters, and camphor and plasticizing materials are added. The mixture is formed into thin sheets on drums and cut into narrow strips after having been coated with a gelatin emulsion containing silver halides. Because of the danger of fire there has been an increased demand for "safety film" made from cellulose acetate, which burns only very slowly. Somewhat thinner sheets are made not only from cellulose acetate but also from cellulose xanthogenate, and are extensively used as transparent wrappings for merchandise.

Coated Fabrics. Cellulose esters, both nitrates and acetates, are mixed with pigments, dyes, vegetable oils, and solvents to form a thick, viscous liquid called "dope." This is spread on fabric, and the excess removed by scraping blades. Solvents are recovered by passing the coated fabric over a heated table under a hood connected with a condenser. Embossing rolls give the appearance of leather, and such fabrics are very largely used instead of leather in the upholstery of furniture and automobiles. Inferior grades of genuine leather are often coated with cellulose esters, and imitation of the natural grain of leather is the result of embossing rolls.

Lacquers. Cellulose nitrate of about 12% nitrogen content is soluble in butyl and amyl acetate and similar compounds and in mixtures of alcohol and ether. It has been used for many years as "druggist's collodion," and as a celluloid cement. Such solutions were so dilute that they had no value in lacquers or enamels, and more concentrated solutions were too viscous. Nitrocellulose is now, however, an indispensable ingredient of such protective coatings. This has been made possible by lowering the viscosity of solutions both by changes in the nitration process and by heating the solutions under pressure in pipe coils of acid-resisting alloys with quick cooling, the whole process being continuous. During this operation the product drops about 0.05% in nitrogen content. Until the development of such lacquers, automobile production suffered because of the very slow painting and enameling operations, which meant vast storage facilities while several coats of finish dried. Modern lacquers not only dry very quickly but also give

a more resistant coating to metals and permit the use of more pleasing colors.

Lacquer materials may be divided into volatile substances, which evaporate rapidly after application, and non-volatile substances which go to make up the coating film. Some liquids, such as a number of organic esters, dissolve nitrocellulose directly. Neither alcohol nor ether is a nitrocellulose solvent, but a mixture of the two dissolves the type of nitrocellulose used in lacquers quite readily. In recent years the "two-type" solvents have been developed, which are at the same time alcohols and ethers, and are known as glycol ethers. "Cellosolve" is diethyl ether in which one hydrogen on the end carbon of one ethyl group is replaced by hydroxyl, $\text{CH}_3\text{CH}_2\text{—O—CH}_2\text{CH}_2\text{OH}$. The volatility of such substances is considerably lowered by their alcoholic nature. If the materials that evaporate are too volatile, there is marked cooling accompanied by condensation of water with consequent whitening and dulling of the films. Solvents include a variety of alcohols, esters, ketones, glycol ethers, and a considerable number of hydrocarbons, both aliphatic and aromatic.

A nitrocellulose film wrinkles in drying and must be made plastic. Softness and elasticity are conferred by certain non-drying oils such as castor oil, and by heavy organic esters such as dialkyl phthalates and triaryl phosphates. Toughness is produced by the nitrocellulose itself, but at the expense of gloss and hardness. These two properties are secured by the addition of limited amounts of a variety of resins, including fossil resins, rosin-glycerin ester, and the synthetic resins of the phenol-formaldehyde, glycerin-phthalic anhydride and polymerized vinyl ester types. All manner of pigments, lakes, and metal powders are used in lacquer enamels. All properties desirable in a protective coating cannot be realized at once, and it is necessary to obtain a balance with preference given to the most desirable quality or cost consideration.

Cellulose acetate may be used in much the same way as cellulose nitrate in production of lacquer with some alteration in materials, both volatile and non-volatile, which enter into the composition of the lacquer. This material has only a very limited use as yet in the lacquer field, but is said to show considerable promise.

Textile Fibers of Modified Cellulose (Rayon). Textile fibers artificially prepared from solutions of cellulose compounds are continuous filaments, and the process by which they are made resembles that which the silkworm uses in that a liquid is forced out or drawn from

a small orifice into a medium in which it forms a filament, which may be of very great length.

The first term applied to such fibers was "artificial silk," since those fibers resembled silk in appearance and general physical properties. The term was not only awkward, but carried with it the stigma of imitation, substitution, and adulteration. In recent years such materials are very generally known as "rayon." The United States Bureau of Standards recognizes rayon by the following definition: "The generic name of filaments made from various solutions of modified cellulose by pressing or drawing the cellulose solution through an orifice and solidifying it in the form of a filament or filaments by means of a precipitating medium." The majority of the firms making such fibers call them rayon, and distinguish fabrics ordinarily made from natural silk by the terms "rayon satin," "rayon taffeta," "rayon velvet," "rayon pongee," etc., when such fabrics are made from modified cellulosic materials. A few firms use other terms. Often the word "rayon" is coupled with a trade name and with the name of the process as well.

Rayon has assumed a definite and very important place in the textile industry. Methods of manufacture have been improved, and chemical research has resulted in a product that is much superior to the materials made in earlier years in wear, appearance, resistance to the action of light, air, water, and cleaning liquids, and in ease and uniformity of taking up dyestuffs.

There are four important methods of making rayon, all of which use cellulose as a raw material. In all cases the cellulose undergoes chemical changes, and the substances formed may be dissolved and reprecipitated in the form of a filament, either by evaporation of the solvent or by the action of precipitating chemicals. In three of the four processes the final product has the same chemical composition and empirical formula as the original cellulose; in the fourth, the product remains as a mixture of cellulose esters.

1. *Xanthogenate (Viscose)*. The general reactions of this process have been discussed already. The cellulose used includes both cotton linters and sulfite pulp. This material is brought to a moisture content of 10%, is cut up, and steeped in an 18% solution of caustic soda. This operation is ordinarily carried out in a horizontal cylinder at one end of which is a plunger functioning as the platen of a hydraulic press. Alkali cellulose is formed, and some of the fiber dissolves. The action of the alkali is allowed to continue for 2 to 4 hours at a temperature of 56° F. to 62° F., after which the contents of

the cylinder are pressed until they occupy one-third the volume of the original dry cellulose. The liquid pressed out of the fiber may be used again, unless it has accumulated sufficient organic matter to injure the product. The alkali cellulose is placed in mixers equipped with serrated saddle and serrated mixing arms and jacketed for cooling. Within 2 or 3 hours this material is reduced to small crumbs which are placed in closed sheet steel cans and kept at a temperature of 75° F. for two to three days. Slight oxidation takes place, and this effect may be increased by adding a small amount of sodium peroxide. The alkali cellulose is then placed in horizontal drums with carbon bisulfide and the drums are revolved until reaction is complete. The crumbs of the plastic solid are placed in mixers, which are essentially jacketed cylinders with stirrers, and dissolved in dilute sodium hydroxide. Several batches are commonly blended to secure the correct concentration. The liquid is allowed to stand for two or three days in well-insulated rooms whose temperature is between 50° F. and 68° F. During this time the larger part of the sulfur splits off in the form of various by-products, leaving only from 1% to 2.5% in the cellulosic material. These changes may be followed closely by the changes in viscosity of the solution. If the material is allowed to stand too long, coagulation begins, which is to be avoided until after filament formation. The liquid is repeatedly filtered, first through presses containing loose cotton between coarse cloth, and finally through very fine-mesh cloth. Air bubbles are removed by keeping the liquid under vacuum for a period of 24 hours in order to avoid breaks in the filament.

The next operation is known as "spinning," which is an unfortunate term, since the word is understood in the textile industry to refer to a combination of twisting and drawing operations as applied to short fibers. As carried out in the production of rayon, spinning means forcing a solution of modified cellulose through a small orifice into a coagulating medium with the production of a continuous filament. Multiple plunger and gear pumps are used. The action in any case is very slow. The liquid goes first through a final filter, which consists of a serrated and perforated pipe wrapped with fine cambric and inside a hard rubber casing, the whole being known as a "candle filter." The liquid passes from a glass "goose neck" through the "spinneret." This is essentially a rimmed cylinder open at one end and with a bottom which has in it a number of properly spaced and very fine openings. The spinnerets may be made of glass, but platinum alloys are more commonly used. The fine stream of liquid coagulates to a filament in a coagulating bath of complex composition, which is very strongly acid

because of the presence of acid salts, mainly acid sulfates. Other materials present include ammonium and sodium sulfates, and various organic substances such as glucose, sucrose, starch, and other carbohydrates. The liquid has been brought to the necessary colloidal condition "with the development of the proper micelle," and the filament is spoken of as a "stiffened colloidal solution." The property possessed by the cellulose molecule of orienting itself lengthwise in films, fibers, and filaments is apparently retained in the modified cellulose. The filament passes through the coagulating bath at the rate of 130 to 200 ft. per minute.

The two methods of handling the very fine filaments produced in the operation include winding them untwisted on a glass or perforated metal bobbin and passing them over a feed wheel and down through a glass funnel into a perforated centrifugal "pot" revolving at 5000 to 6000 r.p.m. As the filaments pile up in the pot, a distinct twist is given them. The bobbin method can be more easily adapted to the production of finer threads, but the pot method is more generally used, since it eliminates later twisting. The fiber is then thoroughly washed and the remainder of the sulfur is removed by treatment with a dilute solution of sodium sulfide (0.75% to 1%). Alkali polysulfides are formed, and the fiber now has the same percentage composition as the original cellulose, corresponding to $(C_6H_{10}O_5)_x$. After various washing, bleaching, and "souring" operations, which resemble those used with other textile fibers, the material is freed of adhering liquid by centrifugal extractors or by drying under tension, and is ready for use.

2. *Cuprammonium*. The cellulose used in the cuprammonium process is mainly in the form of cotton linters, which are treated in kiers with caustic soda or sodium carbonate solutions and bleached. The most common method of producing a solution by the combined effect of ammonium hydroxide and copper compounds is to treat the cellulose with solutions of cuprammonium hydroxide, $Cu(NH_3)_4(OH)_2$. After the cellulose has completely dissolved, the liquid is thoroughly filtered, stored in glass-lined tanks, and stabilized by the addition of sugars and starch. Spinning is now commonly done in alkaline baths, but formerly acid baths were used. If two alkaline baths are used, the first is dilute and the filament is allowed to stretch by virtue of the pull of a falling column as it drops into the second, more concentrated, bath. The product is washed in dilute sulfuric or hydrochloric acid, and both copper and ammonia are recovered. Bobbin and centrifugal

methods are both used, and the subsequent treatment is much the same as in the viscose process.

3. *Nitrocellulose (Chardonnet)*. This is the earliest of all rayon processes. Cellulose nitrate of 12.5% nitrogen content is washed, boiled, shredded, and dissolved in alcohol-ether. After storage to remove air bubbles, the solution is filtered under very heavy pressure through cotton and silk. In the United States the main method of spinning is to force the liquid through spinnerets into the air, where evaporation of the solvent is rapid. The filaments are wound on bobbins, and thence are transferred to spools. They are finally twisted and formed into skeins. It is obvious that a very inflammable material with large exposed surface could never be used as a textile. Denitration is necessary, and this is accomplished in a solution of sodium hydrogen sulfide, NaSH , containing a little sodium sulfide, Na_2S . The product is a modified cellulose.

4. *Acetate*. This process differs from the other three in that the cellulose ester originally formed is used unchanged as a final product. It is the most recent of the four processes, and is an outgrowth of the production of non-inflammable airplane "dopes" and modern safety motion picture film. Purified cotton linters are treated with acetic anhydride, acetic acid, and sulfuric acid. A product representing the maximum degree of esterification, three acetate groups per unit of six carbons, is not soluble in those solvents which are usable. Esterification is carried out to completion, and the triacetate is hydrolyzed to a material approximating a diacetate. This product is precipitated by pouring it into water, and is separated from liquid by filtration. It is washed with water and with sodium bicarbonate solution to remove all traces of acids, and again with water to get out sodium acetate. The dry acetate is added to acetone in a mixer, and after filtration, storage, blending, and removal of bubbles, the liquid is pumped through spinnerets. Since the liquid is non-corrosive, practically any hard metal may be used for the spinnerets. The filament is spun into the air, passing some 15 ft. from the spinneret through warm air before reaching the bobbin or centrifugal pot. The application of dyes to cellulose acetate rayon presented a difficult problem, which was ultimately solved both by improved methods of dye application and by the development of new dyes suited to this type of fiber. Acetate rayon is particularly adapted to what is known as "cross dyeing." It is possible to mix two dyes of different color and chemical nature and place in the dye bath a fabric made up of this variety of rayon and

another type of fiber. Acetate rayon fibers will take up the color of the dye for which it is adapted, and the other fibers the other color. Some very beautiful color effects are thus possible.

Artificial wool is made by combing, carding, and spinning the short ends of rayon; artificial horsehair is merely a heavy rayon filament; and artificial straw is made by extrusion through a slit instead of a fine circular orifice. The high lustre of ordinary rayon may be reduced to any desired extent by chemical treatment. One of the drawbacks of the earlier rayons, which is now being eliminated to a considerable extent, was loss of tensile strength when wet. Rayon absorbs water but does not mildew, and is not acted on by perspiration. This material, like cellulose, is sensitive to hot alkaline solution, but is resistant to short exposure at moderate temperatures. Inorganic acids must not be dried in rayon, but organic acids may be so applied to give the rustle or "scoop" of weighted silk.

The price of rayon is higher than that of cotton or linen, but only about one-third that of silk. Although there has been very little growth in the silk industry, rayon seems to have developed for itself a new market, since its production has increased at a very rapid rate. In 1926 the world production of rayon was around 200 million pounds, and of this, 60 million pounds were made in the United States. By 1928 the world production had increased to 350 million pounds and the share of the United States was 100 million pounds. In 1930 the United States production was estimated at between 120 and 125 million pounds. Viscose rayon represents fully 80% of all production. It is estimated that about four times as much rayon is produced as silk. Compared with the vast bulk of cotton, the quantity of rayon which is made seems small, since more than 14 billion pounds of cotton find their way into textiles, while wool production is 3 billion pounds and linen 2 billion pounds. The rate of growth of rayon production indicates that it is a material destined to a still larger use.

Vulcanized Fiber. The term "vulcanized fiber" is entirely misleading, being applied to a partially hydrolyzed cellulose material merely resembling completely vulcanized or hard rubber. This material is made by subjecting paper to the action of warm, concentrated zinc chloride solutions for a very short time. The surface of the paper gelatinizes, and if exposure were long enough, complete solution would take place. The paper is wound on a drum as it is treated, and is pressed by a roll during the winding. The surfaces fuse together, forming a homogeneous mass of fiber. The zinc chloride is removed by a long period of washing. When this material has dried, it is very

hard and resistant to solvents and chemical reagents. It has a very high electrical resistance, and can be cut and turned like wood. It thus has very extensive use in making electrical equipment. Vulcanized fiber is a widely applicable material of construction, examples of its use being trunks, containers, and the bodies of small factory trucks.

III. Distillation Products of Cellulose

The cellulose material that is commonly subjected to destructive distillation is wood.

Hardwood Distillation. The distillation of hardwood was begun in order to prepare charcoal for use in metallurgy. In the earlier stages of charcoal production no by-products were recovered. The wood was merely piled up and covered with earth to prevent combustion, and the upper portion of the pile was destructively distilled by the burning of a part of the wood at the bottom. With an increase in the demand for acetic acid, methods of by-product recovery were naturally developed. Practically every hardwood may be used, but the varieties mainly employed are beech, birch, hard maple, oak, ash, ironwood, hickory, and chestnut. The wood is not selected by species, except that softwoods are excluded. Most of the material used is that which is not fit for the lumber industry, such as twisted trunks, tops, branches, and second-growth timber, along with logging slabs and sawmill waste.

Hardwood may be heated in the absence of air to 250° C. before there is any amount of chemical reaction. Decomposition begins around this point, and what may be spoken of as "primary tar" is driven off. This material does not survive contact with the heated surface of the wood and that of the metal ovens, but breaks down into gas and liquids, which go to make up the materials recovered in commercial practice. These decomposition reactions are exothermic to such an extent that the heat balance of all reactions shows a slight evolution of heat. The gas that escapes during distillation is about half carbon dioxide and half combustible substances, largely carbon monoxide with smaller amounts of methane and other hydrocarbons. Condensable substances that are driven off are mainly acetic acid, methanol, and tar, together with minor amounts of formic acid, methyl acetate, acetone, and allyl alcohol. The higher-boiling material may be separated into wood oils, wood creosote, and hard pitch. The residue left in the oven is mainly carbon, and is known as wood charcoal.

The wood contains from 15% to 20% water before it is in what is called "air dry" condition, and is ready for distillation. The bulk of the wood to be distilled is dried in long tunnels of brick or concrete, heated by the waste boiler stack gases. The wood is usually cut into 4 ft. lengths, or blocked to 1 ft. lengths and split to 3 or 4 in. maximum diameter. After screening, the wood is dropped into cars made of steel slats on low trucks called "buggies," which will hold about two cords of wood. These buggies pass through the dryers unless the wood has been previously conditioned by standing in the open.

From the dryers the wood passes into ovens, which are cast iron chambers averaging more than 50 ft. long, and about 50 sq. ft. in cross section, being slightly higher than they are wide. They are set in brick chambers, and to provide for expansion and contraction are suspended from steel beams supported by surrounding brickwork. The doors at each end are wedged on to make the ovens practically air tight. From three to five buggies are placed in an oven for a run. Ovens are usually parallel in pairs so that a single brick partition may take the place of one outside wall for each chamber. Each oven is heated mainly by coal fires in one or two furnaces. By the use of flues and arches the hot gases are made to pass along under the ovens, around their sides, and over their tops. Since the doors are not heated, they are protected by storm doors to prevent condensation on their inside surfaces.

After a charge has been run in on tracks and the doors wedged in place, heat is gradually applied until a maximum of 250° C. is reached. For the first 4 hours the condensate is largely water. As distillation progresses, the color of the condensate and its acid content increase. Within 8 to 10 hours tar begins to appear. By this time the exothermic reactions have begun to take place at such a rate that only a small amount of heat is applied to the oven, and by the end of the operation a temperature of 400° C. has been reached. Temperatures are measured and controlled by pyrometers. The distillation period is from 16 to 30 hours, according to the age and the extent of previous drying of the wood. This is followed by a 2-hour cooling interval. The ovens are discharged by opening the doors and pushing the cars of charcoal very quickly into long, sheet-iron cooling chambers, which are air tight, and at the same time another charge is placed in the oven. The charcoal is quite hot and catches fire when it comes into the air, but burning is checked as soon as the cooler doors are closed and ceases as soon as the oxygen in the cooling chamber is exhausted. After 24 hours in the first cooler, the partially cooled charcoal is passed

into a second cooler for another 24 hours, after which it is held on the buggies in an open shed for three days before shipment.

In addition to the distillation of cord wood, waste in the form of chips may be subjected to a similar process. The method employed for distilling wood chips in one large plant involves drying the wood in rotary dryers at a temperature of 600° F. to less than 1% moisture content, and feeding them while hot into a vertical insulated retort some 10 ft. in diameter and 40 ft. high, lined with 18 in. of firebrick backed up by other insulating materials. The exothermic reactions taking place farther down in the chamber bring the fresh charge up to a still higher temperature. The temperature in the retort varies from 260° C. (500° F.) at the walls to 316° C. (950° F.) in the center. Insulation prevents escape of most of the heat, and the process of distillation is continuous. A slight pressure (2.5 mm. of water) is maintained in the retort. As the charge works down and is converted into charcoal, fresh chips are fed into the top. In order to get the charcoal to the temperature of the outside, it must pass through continuous coolers, which are sprayed with water, and through conditioners, which are like the coolers, but in which the heat removed is that developed by the charcoal taking up oxygen from the air. The yields of methanol and charcoal are lower than in the oven process; the crude acetate of lime produced is about the same but is higher in formates. The gases that escape are about the same volume, but have twice the calorific power of oven gases.

Returning to the oven process of hardwood distillation, the disposition of the products may be described.

The gases and vapors from the ovens pass through condensers of copper built to care for maximum production. Fixed gases are separated without scrubbing, and ordinarily they are burned under the retorts where they were made. Some plants scrub the gases, feed them to a common main, and burn them under those retorts where they are most needed. This gas has a heat value of a little less than 300 B.t.u. per cubic foot, and represents around 15% of the weight of the wood.

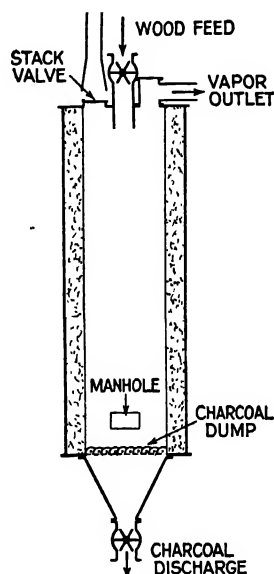


FIG. 115.—Stafford Retort for Distillation of Wood Chips. Courtesy Professor O. F. Stafford, University of Oregon.

The condensed liquids, known as "pyroligneous acid" or "green liquor," separate in settling tubs into two layers, the upper one being largely a water solution and the lower a heavy tarry oil. The water layer contains some dissolved tar, and the tar carries considerable water. The tar is placed in closed wooden tanks and treated with steam in order to drive out acetic acid and methanol. This also drives out some oils, which may be separated because of their immiscibility with water. Most wood tar is used as fuel, but a portion of it is refined in separate plants. The products of the distillation of wood tar include: wood oils, which are a source of some valuable solvents; creosote oils, used as flotation oils, stains, wood preservatives, and medicinal products; and a residual pitch, whose high dielectric constant makes it valuable in transformers and oil switches, and whose binding power makes it an excellent filler in compounding rubber.

The aqueous layer from the settling tubs is given a preliminary distillation, either in single stills of copper with closed steam coils, or in regulation multiple effect evaporators. Some light oils will naturally pass over during the evaporation, but the bulk of the oils and tar remains behind in the evaporators, and may be removed at intervals by the combined effect of heating coils and injected live steam and added to the main portion of the tar.

The condensates from the steam-treated tar and the evaporators are settled and mixed. They contain acetic acid and methanol, together with smaller amounts of methyl acetate, acetone, and allyl alcohol. The first step in separating these substances is neutralization of free acid by calcium hydroxide. A sludge separates and is either settled or filtered out. By use of modern distillation methods the clear liquid may be separated into an alcohol-free acetate solution, fractions consisting of 92% to 95% methanol, and a series of mixtures used as solvents without separation. Various constant boiling mixtures, such as acetone-methanol and methyl acetate-methanol, are formed, which require chemical methods of separation involving chlorine and caustic soda. Hence it is cheaper to allow some methanol to remain in these mixtures than to attempt complete recovery. The methanol from this distillation is refined in column stills to a maximum purity of 99.9% with less than 0.05 acetone present.

The solution of calcium acetate is concentrated in multiple effect evaporators to a point just short of crystallization, and this liquid is converted to a paste of crude calcium acetate on steam-heated drums. This paste is removed from the drums by woven wire belts, and carried

in festoons through a dryer heated by waste flue gases. The dry calcium acetate is removed by tapping the belt. It finds its chief use in making acetic acid. This is made by stirring and heating crude calcium acetate with sulfuric acid of such a concentration that calcium sulfate dihydrate is left behind and the distillate is about 35% acetic acid. This may be concentrated by the use of column stills to the constant boiling mixture, and this in turn by freezing produces anhydrous acetic acid. Acetone can be made by heating crude calcium acetate, and for many years this was common practice, but acetone is now made more cheaply as one of the final products of the fermentation industry. Acetone and butyl alcohol are produced in one process of starch fermentation. Oxidation of isopropyl alcohol also results in acetone.

The method used in one large plant, which handles wood chips in vertical retorts, omits the neutralization of the acid distillates from the settled pyroligneous acid, and sends these distillates to continuous stills with columns, which yield crude 95% methanol at the top and a 15% acetic acid at the bottom. The crude methanol is put through a refining process, which ultimately yields "c.p. methanol," together with allyl alcohol, methyl acetone of 75% grade, a 75% methyl acetate, and "alcohol oils." The dilute acetic acid is used directly in making ethyl acetate.

Other plants scrub acetic acid from a mixture made up of steam and vapors of acid, alcohol, etc., by means of high-boiling wood oil. The scrubbing is carried out by running the oil down a bubble tower to meet the vapors from the distillation of pyroligneous acid. The solution of acetic acid in oil is dehydrated in a second tower, and the acid is removed under reduced pressure.

Yields per ton of seasoned wood are of the order of 600 lb. of charcoal, 5000 cu. ft. of gas, 5 gal. of "spirits" of which a little more than 60% is methanol and nearly 20% is methyl acetate, 100 lb. of acetic acid in terms of 100% material, and 11 gal. of tar.

The hardwood distillation industry finds itself surrounded on all sides by formidable competition. Charcoal is no longer in such great demand in the steel industry or as a domestic fuel. Acetic acid is a product of the calcium carbide industry. Acetone has given way to some extent to newer synthetic solvents, but the more active competition in this market is due to the acetone made along with butyl alcohol by the fermentation of starch. Methanol is being made successfully in large quantities by high-pressure combination of hydrogen and carbon monoxide, both derived from water gas.

Resinous Wood Processes. The primary object of the distillation of resinous wood, mainly pine, is to obtain turpentine, oils, and tar, and hence the process is hardly to be classed among cellulose industries. Distillation is complicated by the insulating effect of the wood fiber as well as by the presence of rosin. Destructive distillation of resinous wood causes the decomposition of rosin, a coke forming in the pores of the charcoal, which distinguishes this product from hardwood charcoal. No acetic acid or methanol are produced, the valuable products being turpentine, pine oil, tar oils, and pine tar.

In order to complete the picture it is necessary at this point to discuss very briefly other methods of utilization of resinous wood, primarily pine. When the sap wood of the living pine tree is chipped there results an exudation of a liquid. Distillation of this material produces turpentine as the distillate and pine rosin as the residue in the still. Waste wood, particularly old stumps and dead limbs, is the source not only of turpentine and rosin but also of a product not obtainable from the sap wood of the living tree, namely pine oil. This material is present only in the heart wood. The method of obtaining these three substances includes chipping or shredding the waste wood, passing steam through the chips to obtain turpentine and some of the pine oil, and finally extracting the chips with gasoline to remove the remainder of the pine oil and the rosin. The turpentine is refined by the action of sodium hydroxide or sodium carbonate solutions followed by steam distillation. Some of the rosin is refined by a variety of processes, among them being vacuum distillation.

Fully twice as much wood is handled by the combined steam and solvent process as by destructive distillation, and the larger part of the turpentine and rosin of commerce comes from living trees.

CHAPTER XXII

PROTEIN INDUSTRIES

Proteins are complex organic compounds made up primarily of carbon, hydrogen, oxygen, and nitrogen. The proportions of the elements present vary considerably, but may be represented with fair accuracy by the following limits:

	PER CENT
Carbon	51-55
Hydrogen	6- 7
Oxygen	20-24
Nitrogen	15-19
Sulfur	0.3-2.8
Phosphorus	0.4-0.8 (when present)

Other elements, when present at all, are only in such small amounts as to be spoken of as "traces."

Proteins are colloidal in their physical state, and do not form true solutions. They decompose on heating so that molecular weight determinations by solution and vapor pressure methods are impossible. Proteins are amphoteric in their chemical nature, since they react with both acids and bases. Thorough hydrolysis of proteins yields amino acids. Some twenty different amino acids have been isolated as a result of years of study of protein chemistry by a large number of investigators. Obviously not all of these acids are found in the hydrolysis products of every protein. These acids include monobasic monoamino acids, dibasic monoamino acids, hydroxy and thioamino acids, heterocyclic amino acids, and aromatic amino acids. Proteins may be regarded as made up of a large number of amino acid units, whose amino groups are linked to carbonyl groups as acid amides. Ring complexes of the general nature of diketopiperazines, as well as straight chain compounds, are probably present in proteins. Asymmetric carbon atoms increase the complexity of protein chemistry.

The physical chemistry of proteins has been extensively investigated and much information has been obtained that is useful in industry, but there yet remains an infinite amount to be learned in this

field. The relation of hydrogen ion concentration to the physical properties and behavior of proteins is of extreme importance. The swelling of proteins in water is a function of the hydrogen ion concentration. There is a definite connection between the stability of colloidal protein gels and the potential difference at the film boundary between the protein and the liquid surroundings. When a protein has an equal number of positive and negative electrical charges it is said to have reached the "isoelectric point." For gelatin this is attained in a suspension which has a *pH* value of 4.7. Some investigators visualize protein molecules as made up of an intimate lattice work of crossing chains of molecules.

Food materials may be divided into three classes: carbohydrates, fats, and proteins. Animal life can be prolonged indefinitely on a diet from which both carbohydrates and fats are absent, but life cannot be sustained for any length of time without proteins. Those food industries in which protein materials predominate include meat packing and canning, baking, vegetables, and dairy products. Relatively few chemical changes take place in the manufacture of food products in general. Those changes which do take place in cooking are not well understood, and matters of taste, flavor, appearance, and keeping qualities govern the processes of food products. Modern food industries are increasingly employing the processes, methods, and equipment of chemical engineering. Protein industries, aside from foods, include textile fibers of animal origin (wool and silk), casein, gelatin, and leather.

WOOL

Animal hair is made up mainly of a complex protein known as "keratin." It is particularly distinguished by its high sulfur content, which is from 2% to 4%. Wool is the most important of hair materials used in textiles. Wool is not acted upon by dilute mineral acids. Vegetable materials may be removed from raw wool and cotton fibers from waste cloth made of both cotton and wool by the use of dilute sulfuric acid or aluminum chloride solutions. Sulfuric acid in small quantities may be dried into wool to increase its sensitiveness to dyes. Nitric acid gives wool a permanent yellow color because of the formation of chemical compounds which bear the general name of "xanthoproteic acid." Dilute caustic soda solutions (3% or less) at boiling temperature will rapidly destroy wool, and higher concentrations dissolve wool at lower temperatures. Prolonged exposure to very dilute solutions of sodium hydroxide causes a partial fusion of the outer

surface and a shrinkage in the size of the fibers. This explains why soaps containing an excess of caustic soda cannot be used with wool, and why boiling with any sort of soap causes shrinkage. Wool is able to adsorb a number of metallic salts, this property being of particular importance in the application of mordant dyes.

Wool, like other animal hairs, is made up of a series of short cells surrounded by longer cells and sheathed by overlapping scales. This roughened surface makes possible the manufacture of felt, which is essentially a mass of tangled fibers rather than the product of twisting and weaving operations. The dyeing of wool is due primarily to the penetration of the dye solution or suspension into the short cells lengthwise of the fiber, and diffusion outward into the long cells and the outer scales. Only by the use of mordants, or substances which are adsorbed by fibers and which themselves adsorb dyes, is it possible to cause wool to take up dyes on its outer surface.

The preparation of wool for use as a textile fiber involves removal of undesirable accompanying materials. The fleeces are first graded and sorted. Crude wool carries large amounts of wool grease, adhering dirt, and soluble salts resulting from dried perspiration. It is commonly washed in warm, soft, soapy water, being carried through a series of tanks with intervening squeezing by rolls. The wool loses some of its elasticity and about 10% of its tensile strength during this treatment. Some progress has been made in cleaning wool with organic solvents, but their use is still quite limited. The fiber contains an oil which is inside the sheath of scales, and which renders the hair pliable. This should not be removed in the washing operation.

The soapy washings may be mechanically freed of wool grease, but such effluents are processed in most cases solely to prevent stream pollution. Wool grease can be more easily and profitably obtained from naphtha extracts, and a product of greater purity results. The wool grease is refined and the final product is lanolin. From 70 to 100 lb. of potassium salts are recoverable from each 1000 lb. of wool; when the price of potash was high, some of this material found its way into the fertilizer market.

SILK

The fiber of silk is produced by the exudation of a liquid from the head canals of the silkworm, the liquid solidifying to a flexible filament immediately after being exposed to the air. The liquid comes from two parallel canals, forming two filaments, which are immediately cemented together and covered by silk glue, which comes from two

other canals. The filament proper is made up of "fibroin," which is a little less than three-fourths the whole weight of the silk. The cementing material is "sericin" or "silk glue." Fibroin is not affected by soapy water, but the sericin is peptized by the soap and passes into colloidal suspension. The rate of removal is slow, and the amount taken off depends on the time of exposure, the concentration of soap, and the temperature. The colloidal suspension of sericin, after some treatment, is used as a component of the dye baths in which silks are given their final color.

The fiber of silk, being primarily protein, is quite sensitive to alkalies and relatively resistant to dilute acids. The amount of sulfur present is quite small. In addition to proteins the silk fiber contains 4% to 5% of other organic substances, largely fats and carbohydrates, and a little mineral matter. Silk will adsorb metallic salts very readily, especially those of iron and tin in amounts equalling the weight of the fiber. This process is known as "weighting." Reputable silk mills use no more metal salts than are necessary to give definite effects in the cloth, which include wearing qualities and improved appearance after dyeing.

The cultivation of silkworms is a great industry in the Mediterranean countries and in parts of the Orient, particularly China and Japan. Eggs are laid by the silk moth on strips of cloth, which are then kept in rooms for several months under carefully regulated conditions of temperature and humidity. About a month before the worm is to be hatched from the egg, the temperature is raised from the dormant to the incubation value. When the worm hatches it is about 3 mm. in length and weighs about 0.5 mg. This thread-like worm is fed on mulberry leaves, and after 40 days it has increased in size and weight about ten thousand fold and is ready to spin its cocoon. The movement of the head of the worm lays down the filament in the form of a tiny figure 8, and successive rows of these form the cocoon, in which the worm seals itself. The outer layer, which is obviously formed first, is attached to a twig. When the cocoon is complete, the worm passes into the pupa or chrysalis state. Inside of three days the chrysalis turns into a butterfly or moth, and cuts its way out of the cocoon. To prevent the cutting of long, continuous filaments the cocoon is heated to 60° to 70° C., to kill the worm. The cocoons are put into warm water to soften the silk glue, after which the filaments are unwound, those from several cocoons being reeled off and twisted together into a thread, and finally made up in a skein. A single fiber varies in cross section from an ellipse to an irregular polygon, some-

times even being triangular. Individual crude silk fibers are about 0.018 mm. maximum diameter; they may attain a length of 1200 meters, and are rarely less than 350 meters in length. Most crude silk is a cream color, but some silks are a brilliant yellow. This color is entirely lost in the subsequent degumming operations.

In the process of unwinding the cocoon, the portion that is attached to the twig must be gotten off before a continuous filament can be secured. This short-length material, known as "frissons," is baled and sold at a reduced price for making silk yarns, which work up into a somewhat weaker thread. There are also cocoons that are pierced, since a certain number of moths must be allowed to escape for purposes of propagation. These cocoons may also be used in the silk industry.

Reel silk is treated with a little vegetable oil to render it pliable, after which it is made into thread, and sometimes into woven fabric, before it is degummed, either partially or completely. Frissons and pierced cocoons are degummed as the first step in their passage through the silk mill, being steeped in warm, soft, soapy water, washed, and centrifuged. The conversion of the pierced cocoons into clean fiber involves a complicated process of drawing out, combing, and carding. Ultimately this type of silk, known as "spun" or "floss" silk, appears in much the same form as carded cotton or wool, and is ready for spinning into yarn and thread.

The relative sensitiveness of protein and cellulosic substances to acids is taken advantage of in producing designs on velvets. The pile of such velvet is made of rayon and the basic fabric is silk. A design is printed on the velvet with a paste that contains aluminum chloride. Steaming causes partial hydrolysis of the aluminum chloride with the formation of hydrochloric acid. The rayon dissolves wherever the paste has touched it, leaving a sheer fabric with a pattern in unchanged velvet. These materials are known as "cut brocade."

CASEIN

The principal protein found in milk is casein. It is somewhat acidic in its nature, and in milk is associated with calcium as "calcium caseinate." The albumin of milk, "lactalbumin," serves as a protective colloid to prevent coagulation. When this is destroyed by the specific enzyme, rennin, the calcium derivative of casein precipitates. Free acid precipitates the free protein. The isoelectric point of casein is at a pH of 4.6. Commercial cheese is produced by the coagulation

of calcium caseinate and subsequent bacterial changes. The casein content of milk is about 3.5%, and it represents about four-fifths of all proteins present.

Casein is prepared commercially from milk by removing the butterfat by high-speed centrifuges, faintly alkaline solutions being necessary, and the coagulation of the casein by dilute acids. Rennin has a limited application in the casein industry. Buttermilk casein is of lower grade with the exception of that made from "sweet cream" buttermilk. The casein is washed, drained, pressed, ground, and dried in vacuum dryers of either the rotary or shelf type.

In addition to being present in such food products as cheese, milk powders, and special "reconstituted" or synthetic foods, casein finds very extensive use in industry. Many cold-water paints employ casein as a binder along with such substances as lime, aldehyde ammonia, and hexamethylenetetramine to render the casein insoluble, and pigments, colors, and fillers. Casein is used in the preparation of coated or "enameled" papers. Casein plastics are composed of casein, plasticizers, dyes, pigments, and fillers, the casein being hardened by treating the finished products with formaldehyde solutions. A transparent product may be obtained by dissolving the casein in alkali, but translucent products are commonly made by using powdered casein, the mixture being moistened and rendered plastic by heat and pressure. Mottled and streaked products are made by adding fragments of previously hardened material to the powder. The time required for hardening is from two weeks to six months. Casein "glues" or adhesives usually contain lime, and are used in the woodworking industries.

GELATIN

Gelatin is derived from "collagen," a protein substance found in the skins and bones of animals. Collagen in the bone serves to prevent crystallization of calcium phosphate and calcium carbonate. The term "ossein" is also applied to bone collagen. Cartilage contains "chondrigen," from which "chondrin" may be isolated. This in turn may be broken up into mucin and collagen. Skin and other connective tissues have collagen as their principal component.

If carefully made from selected raw materials under clean conditions and without introduction of harmful substances, gelatin is a food product. It forms jellies of varying consistency, but is not an ingredient of pure fruit jellies, which owe their physical properties to a carbohydrate known as "pectin." Food gelatin prevents formation of

large ice crystals in frozen desserts, and also renders milk more digestible by preventing the formation of large casein curds by gastric juice with the accompanying occlusion of fat. Powdered gelatin, sugar, the solids from evaporated fruit juice, colors, and flavors are the ingredients of the popular dessert powders.

Technical gelatin has a great variety of uses, including adhesives, ingredients of sizing and stiffening compositions, colloidal protectors in electrotyping, refining, and plating, and in making the emulsion of silver salts used in photography. The efficiency of photographic gelatin depends largely on its content of sulfur-containing compounds, for example cystine or allyl thiocyanate, the latter probably originating in the animal's fodder. These compounds form colloidal nuclei of silver sulfide. Crude gelatin is used very largely as an adhesive and is known as "glue." This term because of similitude of use has a rather broad application to all sorts of adhesives regardless of their chemical composition, being used to designate carbohydrate gums, soluble silicates, casein materials, and synthetic resins.

The main sources of gelatin are bones, raw hides, sinews, and scrap leather. Bones must be steamed as free of grease as possible, after which they are ground and freed of remaining grease by organic solvents, and are finally leached by hydrochloric or sulfurous acid, this treatment leaving collagen as a residue. Phosphates are recovered from the acid extract by addition of a suspension of calcium hydroxide followed by filtration. Chrome tanned leather scrap may be detanned by acids such as oxalic, after which it is handled as ordinary hide stock. Both hides and sinews are treated for a long time with a saturated solution of calcium hydroxide, which swells the protein fibers and causes the separation of mucin. Bleaching is effected by hydrogen peroxide or sulfur dioxide. The lime is removed by washing, neutralization, and further washing.

These different treatments all yield relatively pure insoluble collagen, from which gelatin is made by the use of hot water. The temperature in the open-tank process is not allowed to go above 70° C. Gelatin may be extracted in closed tanks under slight steam pressure, stronger solutions being obtained, but at the expense of the binding power of the glue. Care must be taken not to degrade the gelatin into undesirable hydrolysis products. The whole process is essentially an extraction with hot water. When specific gravity and chilling tests indicate a satisfactory product, the colloidal solution of gelatin is withdrawn and fresh water put into the tanks or autoclaves, the process being repeated as long as yields justify.

The extract is clarified by filtration, by centrifuging with filter-aids, by the use of alum, or by phosphoric acid and lime. When sulfurous acid is used with bone stock, lime produces calcium sulfite as a clarifying agent. Chemical clarification tends to reduce the binding power of glue.

The clear gelatin solution is concentrated by evaporation, usually under reduced pressure in multiple-effect film evaporators. The concentrated solution may be chilled to a jelly which is cut into sheets, and these sheets dried on nets in tunnel dryers, or it may be carried completely to dryness in rotary or drum vacuum dryers. Gelatin solutions may also be spray-dried, or they may be chilled in non-aqueous liquid to globules, which when dried yield "pearls" of glue.

Glue appears on the market in sheets, flakes, pearls, or powder; the finer grades of gelatin are either powdered or sold in thin sheets. Most of the tests made on gelatin and glue are physical, and include strength of jellies, viscosity of solutions, and water-absorbing power. When glues are to be used for gluing wood, they are sometimes tested for the strength of wood joints which they produce.

LEATHER

Leather is a chemical product of animal skin. Dry skin is chemically stable, but is stiff and hard, and thus practically useless. Moist skin has the necessary qualities of strength and flexibility, but decays readily under the influence of bacteria, and its proteins are readily hydrolyzed. In order to obtain the chemical stability as well as strength and flexibility, certain portions of the skin are removed by chemical processes, and the remaining portions are converted into compounds that have the desired properties by "tanning."

Animal skin is made up of two distinct layers. The upper layer or "epidermis" is quite thin in comparison to the skin as a whole. The thicker lower layer is called the "derma." The skin is attached somewhat loosely to the tissues of the body by what is called "areolar tissue." Adipose or fatty tissue is also between the skin and the body proper, both areolar and adipose tissue constituting the "superficial fascia."

The epidermis has no blood vessels, the living cells drawing their nourishment from the underlying derma. As they grow and subdivide, they are pushed toward the surface, die, and ultimately scale off. Hair, nails, and horns are essentially extensions of the epidermis. The surface of skin is depressed in numerous places, forming pockets or

"follicles." The rapid development of "epithelial" or epidermis cells at the bottom of these pockets causes the formation of hairs. Associated with the follicles are muscle tissue, "sebaceous" or oil glands, and "sudoriferous" or sweat glands. The epidermis, including hair, nails, and horns, is composed mainly of keratin.

The derma also may be considered as made of two layers. The upper portion, which in larger animals is considerably thinner than the

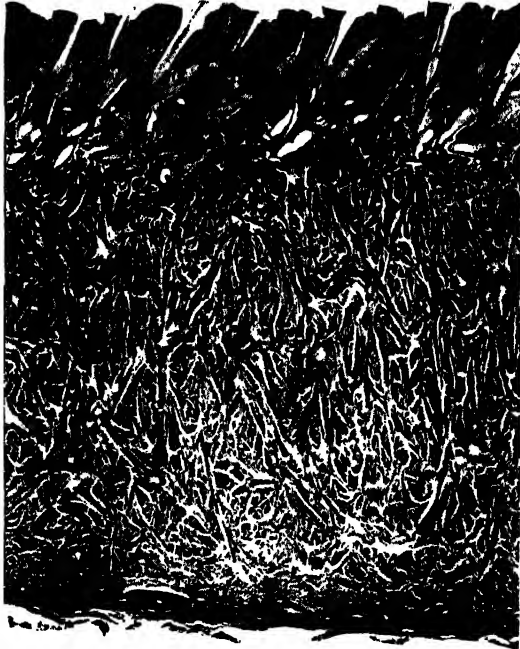


FIG. 116.—Vertical Section of Cow Hide (16 diameters). Reproduced from Wilson's "Chemistry of Leather Manufacture" by permission of The Chemical Catalog Co., Inc.

lower one, is called the "thermostat layer," since it has the important function of controlling body temperature. Its behavior is most interesting and remarkable. When the temperature of the body tends to rise because of exterior warmth, the sweat glands pour their secretions into the ducts, and evaporation of the water of perspiration serves to lower the body temperature. When the outside surroundings are lower in temperature and the body tends to become cold, the "erector pili" muscles contract, and not only close the pores, but break down the oil cells of the sebaceous glands and cause the oil to cover the surface of

the epidermis, thus reducing evaporation. This layer is also distinguished from the lower section of the derma by a considerably greater amount of elastic connective tissue made up of the protein "elastin." Below the epidermis and on the upper surface of the derma is a thin and chemically resistant layer of proteins which are very important in making the "grain surface" of leather.

The lower layer of the derma is made up for the most part of bundles of fibers of connective tissue, composed mainly of collagen. It is also referred to as the "reticular layer," since in many skins the bundles of tissue are interwoven or net-like. Comparatively little elastin is in this layer, but in it are blood vessels, nerves, and varying amounts of adipose tissue containing fat cells. The greater the amount of fatty tissue the lower is the value of the skin for leather manufacture.

Before leather can be made from skin it is necessary to remove all superficial fascia from the inner or flesh side of the skin, and the hair and epidermis from the outer side of the skin. The skin of furs must be tanned without removal of epidermis and hair, and this is accomplished by methods other than those commonly used in making leather. Following the removal of the undesirable materials, which leaves primarily collagen with varying but small amounts of elastin and the important proteins of the uppermost layer of the derma, all these protein materials are converted into stable substances by the process of tanning. The final steps in making commercial leather include various lubricating, dyeing, and finishing operations.

Animal skins are arbitrarily classified according to weight. "Hides" are from full-grown animals of the larger species, and weigh over 30 lb. "Kips" are from half-grown animals of the larger species, and weigh between 15 and 30 lb. "Skins" refer to weights below 15 lb. A bull hide will often weigh over 100 lb., and sheepskins always weigh less than 15 lb.

The main sources of hides are cattle and horses; skins come from calves, sheep, goats, hogs, and the larger varieties of fish such as the shark. Miscellaneous minor sources of leather are the kangaroo, the non-furbearing seal, the alligator, the walrus, and the hippopotamus. That the skins of different animals vary considerably in their structure is evidenced by these examples. The collagen fibers of sheepskin are thinner and less closely interwoven than those of cattle, and often contain an abundance of fat cells in the derma. The fat cells of hog skin extend up into the thermostat layer, so that only a portion of this layer can be used for leather, and even then it is full of holes repre-

senting the hair follicles. The butt or "shell" of a horse hide has a very dense and closely interwoven structure, and is the source of a very durable and solid leather known as "cordovan." The scales of fish correspond to the hairs of warm-blooded animals, and in fish skin the collagen fibers are in parallel ribbons laced together. The surface of shark skin is quite rough, being covered by barbed projections called "hooks," which are removed with the rest of the epidermis before tanning. With the exception of furbearing animals and certain rare types, animals are not slaughtered for their skins, but hides and skins are essentially by-products of abattoirs and packing houses.

Since the use of a knife is apt to damage a skin or hide, removal by peeling is sometimes practiced. Compressed air and a series of mechanically driven hammers have also been employed.

Storage of hides over considerable periods of time is inevitable, and often hides have to be shipped great distances. Thus some method of preserving the skin is necessary. Rapid drying merely seals the exterior and leaves the interior subject to decay, and very slow drying is accompanied by bacterial attack. The most common preservative is sodium chloride or common salt, which not only forms a saturated solution with the water in the skin, but serves to remove a part of the water. The chief occupational hazard in connection with handling hides is from the bacteria and spores of the deadly disease, anthrax; but wet, salted hides rarely have even its highly resistant spores. Formic acid and mercuric chloride are used together and along with salt on hides from anthrax-infested areas.

The cured skins, as they come to the tannery, are usually somewhat shrunken and firm, and must be softened to enable them to be put through subsequent operations. This is most simply accomplished by soaking the skins in cold water, the lowered temperature inhibiting both bacterial action and the formation of enzymes. If cold water is not available, antiseptics must be used. The skin not only absorbs sufficient water to bring it back to its original thickness and restore its pliability, but the water dissolves and removes certain proteins such as albumins and globulins, and some degradation products if the skins have been dried by heat.

When the skins have been restored by soaking to uniform thickness and pliability, all areolar tissue is removed from the derma by means of knives on revolving rollers, a process called "fleshing."

Both the hair and the epidermis must be removed, these operations being known as "unhairing" and "scudding." Since keratin is readily hydrolyzed in alkaline solution whereas collagen is relatively unaf-

fect, the skin is subjected to the action of lime water containing small amounts of sodium sulfide. The younger cells are completely disintegrated, and the outer dead cells and hair are thus loosened so that they may be easily removed. The sulfide functions as a reducing agent, attacking the cystine linkages of the keratin and producing degradation products more easily hydrolyzed in alkaline solution.

A method of loosening the hair now generally abandoned except in the case of very low-grade hides, or sheepskins whose wool is more valuable than the hide, is known as "sweating." The hides are suspended in a warm and humid atmosphere until putrefaction has progressed sufficiently for the hair to be loosened, bacterial action finally being checked by placing the hides in lime water. This process is not only characterized by very unpleasant odors, but is likely to cause considerable damage to the skins.

After the hair is loosened by liming it is removed by throwing the hide over a rubber bolster over which passes a roller equipped with dull knives. The hide is further cleansed by "scudding," in which operation fine hairs, glands, and any remaining epithelial cells in the hair follicles are removed. The hide is scudded over a curved and slanting timber known as the "beam" by drawing a dull two-handled knife over it with the requisite pressure. The fine hairs are removed, and also material in the follicles visible through the semitransparent skin.

During the liming operation a portion of the keratin is decomposed into a material known as "keratose," which remains in the skin. Its isoelectric point is at a pH of 4.1, and thus when the skin is put into the acid tan liquors it is precipitated in the thermostat layer and gives a rough appearance to the surface. The best method of removing the keratose is by means of pancreatin enzymes, the most important of these being trypsin. The operation is known as "bating." Until comparatively recent years the cause of this defect of unbated leather was not known, nor was it recognized that the materials used in its prevention owed their effectiveness to tryptic enzymes. With the modern knowledge of the chemistry of bating, the use of such materials as animal dung has been practically discontinued.

The condition of skin during all operations depends very largely on the presence of salts, and on the hydrogen ion concentration of the liquids in contact with the skin. In order to understand the shrinkage and swelling of skin, it is necessary to relate these phenomena to the general principles of protein equilibrium. According to the Donnan theory of "membrane equilibrium," a definite equilibrium obtains

between two solutions on opposite sides of a membrane that is permeable to all ions of one solution, but not permeable to all the ions of the other solution. The ions naturally tend to go through in pairs or groups of equal numbers of positive and negative ions, but diffusion of the ions that will not pass through the membrane is prevented, and a definite electrical potential is developed. The proteins of skin function with acids as substituted ammonias, and form salts. Within a protein such as gelatin in contact with an acid, hydrochloric for ex-



FIG. 117.—Vertical Section of Calf Skin before Bating (35 diameters). Reproduced from Wilson's "Chemistry of Leather Manufacture" by permission of The Chemical Catalog Co., Inc.

ample, the hydrogen ions and acid ions are free to move, but a part of the hydrochloric acid reacts with the gelatin to form a substituted ammonium chloride, which may be called "gelatin chloride." This substance ties up the hydrogen ion in the substituted ammonium complex. Hence the chloride is present in greater concentration than the hydrogen ion, while outside the protein the concentration of the two is the same. The difference between the ion concentrations inside and outside the jelly constitutes a force which tends to cause ions to leave the jelly. This force is opposed by the attraction between the posi-

tively charged protein complex and the chloride ion. The effect is to pull the protein out into the solution, the movement being apparent as swelling. The degree of swelling is thus a function of the concentration of freely diffusing ions, and very much the same laws and principles apply as in the case of membrane equilibrium.

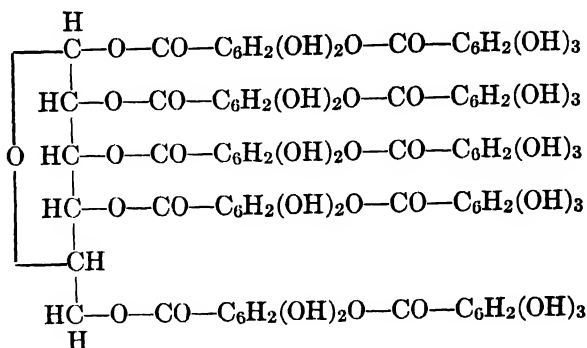
Thus in the case of skin, the hydrogen ion concentration is important not only from the point of view of bacterial and enzyme action, but also as regulating in common with other ions the physical condition of the skin.

Since the common tanning operations are carried out in distinctly acid solutions (pH from 2 to 5), it is often desirable to change the hydrogen ion concentration of the liquid absorbed by the skin to a value nearer that of the tan liquors. There are two methods for accomplishing this result, known as "drenching" and "pickling." Drenching means placing the skins in a liquid containing organic acids such as acetic and lactic. Not only is the desired hydrogen ion concentration attained, but residual lime is removed. Pickling involves the use of mineral acids and salt, is more easily controlled, and is commonly carried out in preparing hides for chrome tanning, or in cases where the damp skins must be stored for any length of time.

Tanning. All that has been said so far has had to do with the preparation of the skin for tanning. Hair and the hardened epidermis cells have been removed on one side of the skin, and the flesh and adipose tissue have been gotten rid of on the other. Undesirable proteins and their degradation products have been removed by hydrolysis, enzymatic action, and solution, and the lime compounds left in the skin by preceding operations have been removed by acid. What is left is essentially the derma, made up mainly of collagen, with varying but small amounts of elastin, and the grain surface proteins. These substances will behave exactly as they would in the raw condition, hardening when dry and decaying when moist. There are two general processes known as "tanning" by which the skin may be converted to the stable protein product "leather." One involves organic compounds known as "tannins," which form compounds with the protein; and the other depends on the action of chromium salts on the proteins to form complex compounds. There are a few minor processes, but the two methods given above produce the greater part of all leather.

Vegetable Tanning. The term "tannin" is applied to a variety of substances that have somewhat the same physical and chemical properties, indicating resemblance in composition and structure. Emil

Fischer and his associates have made a synthetic product isomeric with the tannin derived from Chinese nut galls which has the formula:



Tannins used in making leather are obtained by the water extraction of a variety of barks, woods, leaves, nuts, pods, and roots. Some extracts are partially decolorized before evaporation. Liquid extracts are made by concentration of tannin solutions in multiple-effect evaporators; solid tannin materials are made in single-effect vacuum pans by running the solution to a point where it will solidify on cooling. These materials are rich in tannins, but contain varying amounts of carbohydrates, coloring matter, and other materials that have no value in leather making.

The standard method of evaluation of tannins is with "hide powder." Hide that has been prepared for tanning as described is dried and ground. This powder is subjected to a light chrome tanning. A standard reagent is thus obtained, and the value of a commercial tannin product is determined by the amount of material that can be removed from solution by a given amount of hide powder.

There seems to be a definite quantitative combination between the collagen of the hide and the tannin. The collagen acts as a base in acid solutions, and the tannins are distinctly acidic. It is probable that both nitrogen and oxygen linkages are involved. Tanning greatly reduces the capacity of collagen to combine with mineral acids. The least amount of tannin that will be taken up by 100 parts of collagen is 45 parts, and the maximum is 90 parts. Procter and Wilson consider that there is first an equalization of electrical potential between the surface film and the solution within the hide. The charges of tannin and collagen then neutralize each other, and a stable compound is formed. The practical result is that tanned leather resists the action of air, moisture, and bacteria through a considerable range of tem-

perature, and thus forms a most valuable and necessary article of commerce.

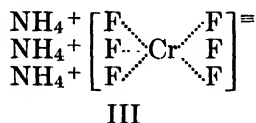
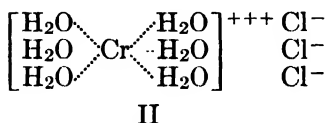
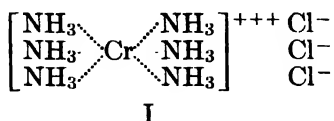
The operation of tanning varies with the thickness of the skin or hide and the kind of leather desired. Spent liquors are made to penetrate into the hide before tanning begins, and by virtue of their acidity to cause plumping or swelling of the fibers. If too concentrated solutions were used at first, the hide would tan rapidly on the outside and penetration to the interior would be prevented. The hides are hung from poles into vats and the tan liquors are circulated so that as tanning progresses a gradually increasing concentration of tannins is attained. Thick material requires still further treatment. Partially tanned hides are placed horizontally in a tank with intervening layers of tan bark, and the remaining space in the tank is filled with strong tan liquors. The time required for complete tanning ranges from a few hours to several months. The process of tanning is followed by cutting off slivers of the skin and noting the depth of penetration, this being controlled by time, temperature, concentrations, and hydrogen ion values.

Chrome Tanning. A very considerable amount of thin leather is the result of a process in which chromium compounds are used. The same effect is gotten in much quicker time than with tannin solutions. The two processes may be combined, a preliminary partial chrome tanning being followed by vegetable tanning, which is accomplished much more quickly by virtue of the first operation. A comparison of the effects of varying humidity on the vegetable- and chrome-tanned leather shows that a change from 100% humidity to perfectly dry air causes vegetable-tanned leather to shrink about 6% whereas shrinkages of as much as 18% are noted with chrome-tanned leather.

Chrome tanning involves the use of basic chromium salts. The old "two bath" process, still used largely for glazed kid leather, involved a treatment of the skins with a solution of dichromate containing hydrochloric acid. The skins were subsequently treated with reducing agents such as sodium bisulfite. Final treatment was with borax solutions. The modern process is referred to as "one bath," and involves the impregnation of the skin by basic chromium sulfate made by reducing sodium dichromate with sulfur dioxide or other reducing agents. Tanning with chromium sulfate solutions takes place at pH values from 2.5 to 3.5.

The action of chromium is explained on the basis of Werner's theory of auxiliary and partial valences. There are three ways in

which chromium may be regarded as functioning in chrome tanning, illustrated by the following type of compounds:



All three types of compounds are probably present in chrome-tanned leather, but the combination of positive nuclei with the acidic groups of collagen is regarded as predominating.

Chrome-tanned leather may be detanned by tartrates and other organic salts, or by acids. This is accounted for by the expulsion of protein groups from the inner sphere by other radicals or complete molecules, or by replacing the acid or basic groups in combination with a chromium nucleus. Fully tanned chrome leather does not shrink as a result of the effect of boiling water. It contains some free acid, and if this is removed, more is formed by hydrolysis of the complex chromium compounds in the leather.

Since most leather is sold by weight, vegetable-tanned leather has the advantage of being much heavier for an equal weight of skin than chrome-tanned leather, the increase being from 40% to 90% for vegetable tanning as compared with 4% or less for chrome tanning.

There are other methods of tanning, which have a very limited use. Alum is used but the leather is not so permanent. White leather used for gloves is alum tanned. Formaldehyde is sometimes used for white leather. The variety of leather called "chamois," because it once was made from the skin of the chamois, is actually made from split sheepskins. The lower layer is used, and is tanned by treatment with cod oil. The oiled skins are bound up and heat is allowed to develop, with alternate periods of cooling and pressing. It is assumed by organic

chemists that peroxide derivatives are formed from the unsaturated glycerides, which combine with collagen, and that lactones from these compounds are adsorbed by the skin. Other materials are used along with vegetable tanning extracts to cut down the rate of combination of tannin with collagen and thus to permit greater diffusion. These are either free lignosulfonic acids from waste sulfite liquor, or synthetic compounds called "syntans," made from phenolsulfonic acids and formaldehyde.

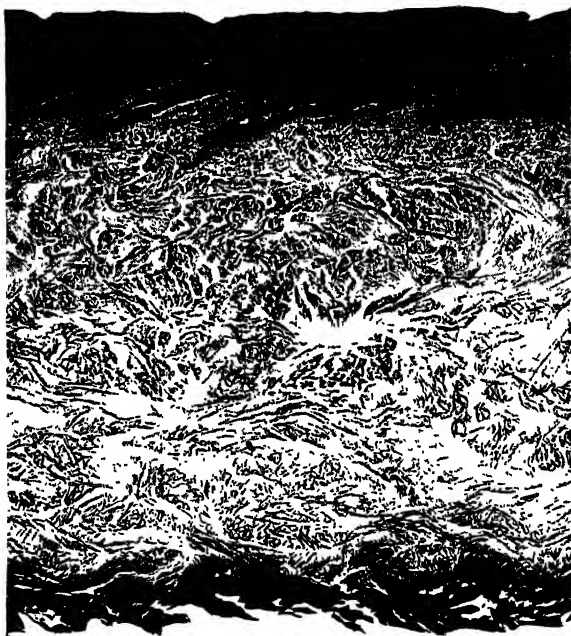


FIG. 118.—Vertical Section of Calf Skin after Chrome Tanning and Finishing (75 diameters). Reproduced from Wilson's "Chemistry of Leather Manufacture" by permission of The Chemical Catalog Co., Inc.

Fat-Liquoring, Coloring, and Finishing. After leather is tanned it is subjected to other operations to make it adaptable to various uses. These operations have to do with pliability, color, surface coating, weight, and resistance to water and steam. It is necessary to work some sort of oil or grease into the leather for lubrication. Pliability may be increased in light leathers by "fat-liquoring," in which the leather is treated with an emulsion made from saponifiable oils and soap, the leather being agitated in tumbling drums. Care must be taken in all operations not to detan chrome-tanned leathers. Heavy

leather may be rendered waterproof by "stuffing" it with grease. Dry leather, particularly chrome leather, is not specially heat sensitive, and the stuffing operation is carried out by heating the leather as high as 90° C. in the presence of grease or oil.

Leather is colored by the use of dyes, and there is much the same control of hydrogen ion concentration, temperature, and dye concentration as in the application of dyes to protein fibers. Uncombined tannin must be removed from the surface of vegetable-tanned leather to prevent its later precipitation in the dye bath. Chrome leather is dyed in an acid bath with acid dyes, and the surface is retanned by means of chromium salts. Acid dyes probably actually combine with both vegetable- and chrome-tanned leather, and basic dyes with the collagen-tannin compounds in the vegetable-tanned variety.

Enameled or "patent" leathers are made by varnishing the surface. Automobile leather upholstery is often coated with a nitrocellulose lacquer. Other coating and finishing materials include casein, albumen, gums, resins, and waxes. A certain amount of finishing material increases the power of leather to repel water from the outside without interfering with the ventilation, which is the power of the leather to permit water vapor to pass from the inside outwards. This is necessary in leather clothing and especially in the uppers of shoes. Those varieties of leather that are sold by weight, such as sole leather, are often weighted with such materials as glucose and magnesium sulfate, which add nothing to the leather but weight and cost, and which are for the most part lost as soon as the leather is wet. A number of mechanical operations are also included in what is known as the finishing of leather, such as buffing, rolling, and embossing.

The by-products of the leather industry include hide trimmings for glue, hair for plaster, spent tan bark for the Dutch process of making white lead or for fuel, scrap leather for fertilizer base goods, and ground leather for compounding in nitrocellulose "dopes" that are spread and rolled on fabrics in making imitation leather.

CHAPTER XXIII

RUBBER

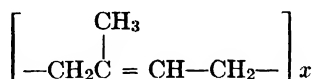
The material known as "rubber" is the basic ingredient of a very great variety of articles of commerce, and is one of the most necessary and useful materials in modern industrial civilization. It may be molded into practically any desired form, and the physical properties of the product can be altered through a very wide range both by the method of treatment and by other substances mixed with the rubber hydrocarbon.

Rubber was known to the natives of South America and the West Indies at the time of the first European explorations. The term "caoutchouc," which is applied to unvulcanized rubber, is derived from a word in one of the Indian dialects that means "weeping tree." The word "rubber" was introduced into common use in the English language by Priestley, since he found that it was being used by draftsmen to rub out graphite marks on paper.

The sensitiveness of rubber to heat limited its use in water-proofed fabrics to very uniformly mild climates. In 1839 the present rubber industry really began when Charles Goodyear, a New England inventor, found that heating rubber with sulfur would produce the "change" which greatly extended the range of temperature within which rubber articles retain their desirable properties. The sulfur chloride, or "cold vulcanization," process for treating thin sheets of rubber to obtain the same effect was patented by Alexander Parkes in 1846. Goodyear also found that large quantities of sulfur would produce hard rubber or "ebonite." These three basic discoveries have made the modern rubber industry possible. Equally important with them is the use of a large variety of organic catalysts to increase the velocity of the vulcanization reaction. The most recent development in the rubber industry is the use of materials that reduce atmospheric oxidation, and are known as "antioxidants."

Chemistry of Rubber. The main component of unvulcanized rubber is a hydrocarbon made up of 88.15% carbon and 11.85% hydrogen. The simplest formula that corresponds to this composition is C_5H_8 .

Rubber is in the colloidal state at ordinary temperatures, but the x-ray indicates its existence, when frozen, in the crystalline state. It is dispersed by organic solvents into a colloidal solution, but gives only a small effect on the freezing point and boiling point of such liquids at low concentrations. Rubber decomposes on being heated, and hence no molecular weight determinations by ordinary methods are possible. It can only be said that the rubber hydrocarbon is a highly polymerized substance of the formula $(C_5H_8)_x$. X-ray studies indicate that rubber may be made up of long chains, probably in spirals. The unit of which the chains are made up is in all probability



The hydrocarbon reacts with bromine, sulfur chloride, ozone, nitrous acid, and other reagents to form compounds indicating one double bond for every five carbons present. Isoprene, 2-methylbuta-

diene, $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \end{array}$, is a very volatile liquid and does not in the least resemble rubber physically. It can be polymerized by the action of various reagents, particularly metallic sodium, into a substance that has some of the same properties as the rubber hydrocarbon, but is not identical with it.

Commercial rubber contains considerable quantities of mineral salts, proteins, and substances called "resins," but its chemistry is primarily that of the $(C_5H_8)_x$ hydrocarbon. Rubber is very stable in the presence of dilute acids with the exception of nitric acid, and is also highly resistant to the action of alkalies.

Vulcanized rubber is not appreciably changed by prolonged exposure to concentrated hydrochloric acid. For this reason, rubber becomes a very valuable material in the chemical plant. Rubber is affected by a number of organic liquids, particularly volatile aromatic hydrocarbons such as benzene in which it swells but does not dissolve.

The rubber hydrocarbon dispersed in water either as a natural or artificial latex bears an electrical charge and can be coagulated into a coating on an anode by the passage of a direct current.

Rubber at 20° C. is tough and highly elastic, but the temperature range over which it retains these desirable properties is very narrow. If chilled to 10° C. it becomes stiff, and with severe cooling it is quite brittle. If heated much above 25° C. it becomes sticky and loses its

elasticity. If the temperature is not too high and the heating is not too long, the rubber returns to its original condition at room temperature. This sensitiveness to temperature changes renders the substance practically worthless from a commercial standpoint except for a few purposes such as crepe rubber soles. If rubber is intimately mixed with sulfur and heated, a change in its properties takes place so that its sensitiveness to heat is greatly lessened. If the amount of sulfur is small, that is 5% or less, the rubber remains tough and elastic and retains these properties over a range of -30°C. to 150°C. If the amount of sulfur is of the order of 25% to 30%, a hard product is obtained. The chief difference between "raw" rubber and the soft vulcanized rubbers containing not more than 5% sulfur is that the vulcanized rubber when stretched returns to its original shape and dimensions, and raw rubber does not. This difference is referred to as "increased resistance to plastic flow." The same effect is produced by the fumes of sulfur chloride, but this treatment is confined to relatively thin sheets, because the penetration is so slow that the outer layers would become quite hard before the interior of the mass is changed appreciably. Any process producing this change in sensitiveness to heat and cold is called a "vulcanization," and because of it rubber is a most important article of commerce. Usually the addition of sulfur is involved in these processes.

Occurrence. In most rubber-bearing plants the hydrocarbon is found in colloidal suspension in water along with small amounts of other organic compounds and mineral salts. Some of these function as protective colloids. This suspension is not a true sap, but is found in a separate cell system, and is known as a "latex." One plant has the hydrocarbon in small particles in the wood under the bark, but this is an exception to the general rule.

Synthetic Rubber. Some progress has been made in producing substances which resemble rubber by the polymerization of butadiene, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, and substituted butadienes, but none of these substances have all the desirable properties of natural rubber, and none can be produced at as low a cost. During a period of greatly inflated prices of rubber around 1912, the announcement of a process of making synthetic rubber, discovered independently by Perkin and Matthews in England and by Harries in Germany, created a great deal of excitement, and considerable money was spent in an effort to make synthetic rubber on a large scale. During the war period a few thousand tons of synthetic rubber were made in Germany, since rubber was contraband and supplies of natural rubber were exhausted. The

main problem was the production of butadienes, which can be made from straight-chain hydrocarbons, from aliphatic alcohols, and from cresols. The production of butadienes could probably be made commercially profitable on a large scale with petroleum as the raw material, but the difficulty that at present appears the most serious is obtaining a particle by polymerization which has the structure and physical properties of the particle of natural rubber.

In addition to isoprene and other butadienes, 2-chlor-1, 3-butadiene, or "chlorprene," has been polymerized to form a substance known by the trade name "Duprene." Chlorprene is made by the addition of hydrogen chloride to monovinylacetylene, which in turn results from the catalytic polymerization of acetylene. It is too early in the development of this product to make any predictions regarding its effect on the rubber industry. At the price of rubber in 1933 it is not possible for this substance to compete, since its cost is very much greater than that of the best grades of rubber.

Duprene is said to have some very valuable properties. The product of the polymerization of chlorprene is a fully vulcanized rubber, so that the use of sulfur is eliminated. It is possible to check polymerization at a stage where a plastic polymer that has the general properties of unvulcanized rubber results. After compounding with pigments, diluents, and other necessary ingredients, further heating results in complete vulcanization. Duprene is quite dense, very resistant to water absorption, to the action of petroleum hydrocarbons and most other organic solvents, and to the action of a number of chemicals, particularly oxygen. It can be gotten into colloidal suspension as a synthetic latex, which permits various impregnation processes. Since Duprene has a number of unique and valuable properties, it may find certain applications in addition to those for which rubber is used.

Wild Rubber. During the earlier years of the rubber industry practically all rubber latex was obtained from tropical forests by native labor. The amount of "wild" rubber now produced is small in comparison with the product of cultivated latex-producing trees. There are large plantations where the trees are grown under carefully regulated agricultural conditions. A very large quantity of rubber comes from the trees of small growers, a fact which makes regulation of rubber production and prices very difficult. Most wild rubber obtained from Africa is from a vine known as *Landolphia*; that from South America is from the tree *Hevea brasiliensis*. The wild Mexican guayule shrub yields a rubber that is quite resinous and is thus of lower

commercial value. The type of tree which furnished practically all plantation rubber is the *Hevea*.

Plantation Rubber. In 1876 Sir Henry Wickham succeeded in smuggling out of the Amazon valley and transporting several thousand seeds of the *Hevea* tree to England, where seedlings were grown in Kew Gardens. A few of these were taken to Ceylon and grown to trees. In succeeding years there was a rapid development in the growth of this type of tree in Asiatic subtropical regions. Plantation growing has recently been started in Brazil, and Africa is also the scene of a recent large rubber-growing project. The following table shows the great changes that have taken place in the rubber industry in the past three decades.

Year	TONS OF RUBBER	
	Wild	Plantation
1900	54,000	4
1909	68,000	3,600
1915	51,000	108,000
1920	40,000	305,000
1929	30,000	813,000

The cultivation of rubber trees of the *Hevea* type requires thorough clearing of the jungle and planting of 120 to 150 seedlings per acre. By the time the trees reach the production stage they are carefully evaluated and the weaker ones removed. Cover crops may be used to keep down weeds if they are not extensive enough to retard tree growth and are also essential to prevent washing out of terraced areas by torrential rains.

Latex. On favorable soil, *Hevea* trees may be tapped within five years, or when the diameter of the trunk is about 8 in. The cell system which carries the latex is just below the outer bark, and is called the "cortex." Immediately below it is a very thin and sensitive layer called the "cambium," and inside this are the sap cells of the outer part of the trunk. In order to obtain latex with the best yield it is necessary to cut nearly through the cortex, and at the same time to leave the cambium intact. The preferred method of tapping employs a cut that is slanting, and is made at such an angle and in such a way that it forms a tiny trough to conduct the latex. Cuts are from a quarter to a third of the circumference of the tree. A spout is inserted

at the lowest point of the cut, and an earthenware, aluminum, or vulcanized rubber cup is placed to receive the latex. At each tapping a strip of bark about 0.05 in. in thickness is taken off on the lower side of the previous cut. In this way the whole surface of the tree for several feet up can be tapped during a period of three or four years without injuring the tree, since the replacement bark grows rapidly and only a small surface is exposed at a time. Yields may vary from 2 lb. of rubber per year for ordinary trees up to 6 lb. per year for bud grafted trees.

The latex obtained from the *Hevea* tree is of much the same nature as that from other rubber-producing plants, and may be regarded as

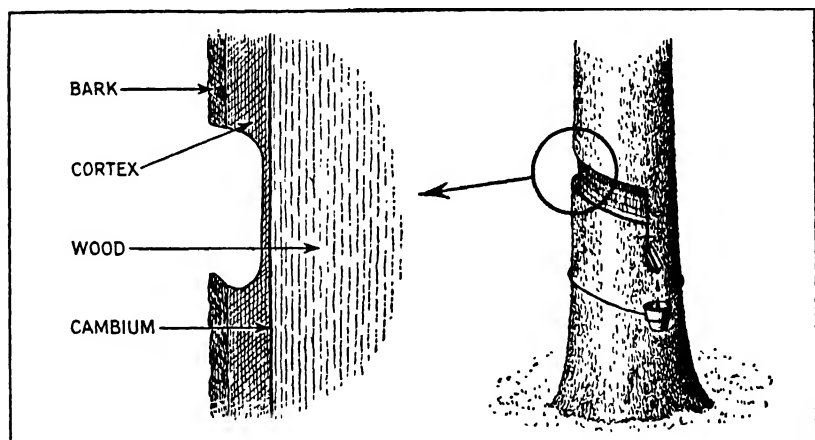


FIG. 119.—Method of Tapping for Latex. Courtesy United States Rubber Company, New York City.

typical. It is a suspension of minute globular particles in a clear serum, and resembles milk in appearance. The particles are approximately spherical but alter their shape under varying conditions in the latex. Some investigators regard them as composed of a tough skin surrounding a semifluid interior. Proteins and resins appear to be adsorbed on the surface of these particles. The particles show a distinct Brownian movement, and are from 0.5 to 3 microns in diameter. They bear a negative charge and thus migrate to the anode when an electric current is passed through latex. The concentration of the hydrocarbon in the latex varies according to the season. In rainy months it may be very low (10% or less), and it reaches a maximum of around 40% except in rather rare cases. Standard latex is 35%. In

the serum are found sugars, "resins," proteins, and inorganic salts to the extent of about 5% to 6%. The proteins serve as protective colloids, but are quite sensitive to coagulants. The so-called "resins" are made up largely of fatty acids, sterols, sterol esters, and minor amounts of miscellaneous organic substances. Some of these materials such as the sterols are natural antioxidants. Latex can be "creamed" by centrifuging or by certain reagents to a 75% rubber content.

Latex is coagulated by any process which destroys the effect of the protective colloid. When latex is allowed to stand without a preservative, particularly at the temperature of the tropics, bacteria and enzymes very rapidly destroy the proteins that act as protective colloids, converting them to acids, so that within an hour the latex shows a distinct acid reaction, and in 24 hours coagulation may be complete. Natural coagulation is not desirable because of the low uniformity of the rubber produced in uncontrolled bacterial development. The smoke coagulation method so widely practiced in connection with wild rubber involves dipping into the latex a pole or paddle and revolving it over a smoky fire. The thin layer of latex coagulates rapidly with accompanying evaporation until a good-sized lump is obtained, which is cut off and transported to market, and is called a "biscuit" or "ham." The effect is not only that of heat but of the phenolic compounds of the smoke, which add preservative value to the coagulating effect of the pyroligneous acid. Certain latices are amenable to creaming or concentration by centrifugal force. The most common method is coagulation by chemical reagents, these being mainly dilute acids. The effect is thus largely that of hydrogen ion on a negative colloid. A weak acid is used so that the effect is more easily regulated and has a wider margin of safety. Formic acid is now most widely used, having largely superseded acetic acid, which was formerly generally employed. The strained latex is mixed with the acid, and when coagulation is complete, spongy masses of rubber are lifted from the clear serum for washing and drying. This material carries with it considerable serum, which is largely squeezed out by rolls during the washing operation. Alum is used to some extent by the natives, but the practice is not recommended.

Spray Drying. In recent years, considerable progress has been made in combining coagulation and drying latex in a spray drying process. Practically all spray-dried rubber is now prepared in the tropics. Anticoagulants are also added to the cups in which latex is being collected from the trees if the material is to be spray dried. Latex is sprayed by means of a rapidly rotating disk into a heated

chamber, and the water is removed so rapidly that the rubber particles are kept cool by the evaporation and are not injured by the heat. It is possible to add sulfur, pigments, fillers, accelerators, and antioxidants to the latex and get an intimate mixture with the rubber hydrocarbon during the drying operation. The main objection to spray-dried rubber is that it is low in plasticity and difficult to process. Spray-dried rubber is said to have some properties not possessed by smoked sheet or crepe rubber; certain antioxidants and accelerators are present in the latex which are lost in the serum in the ordinary method of coagulation. Latex is also used in the direct impregnation of fabrics and the cords of automobile tires with rubber.

Preparation of Guayule Rubber. The rubber hydrocarbon of the shrub *Parthenum argentatum*, or Mexican guayule, is not found in a latex but in particles distributed in the woody structure under the bark. The method commonly employed for guayule rubber is to grind the plant in a ball mill or in a machine which combines disintegration and washing. The finely divided rubber will float to the top, while the fiber, after thorough washing, sinks to the bottom.

Washing. It is necessary to get rubber from any source into the form of a thin sheet before it can be washed and dried successfully. The rubber may be forced between corrugated steel rolls and sprayed with water, but more common practice is first to use the washer-mixer in which two steel rolls run in adjoining shallow troughs. Wild or native rubbers are usually quite dirty, whereas plantation rubber is relatively clean, its condition depending on the care used in its preparation. The washing on engraved rolls removes a part of the non-rubbers as well as foreign matter that may have got into the latex. In one method of preparation, the rubber, after passing through the final rolls, is in the form of a thin sheet of irregular surface, which gives it the name "crepe" rubber. Another widely manufactured form, which involves sheeting and smoking, appears on the market as "smoked sheets."

Drying. Modern dryers use air of a definite humidity on the basis of the rate of passage of moisture from the interior to the exterior of the sheet, and drying is accomplished in a few hours. Sheets of rubber may be dried and smoked at the same time, the effects being much the same as in smoke coagulation. The older method of drying is to hang sheets of rubber in warehouses and lofts and depend on atmospheric drying, but the results are not so uniform or satisfactory as with standard dryers. Drying is necessary to prevent bacterial decomposition of the proteins.

The rubber, after these operations, is now ready for use as a component in making a wide variety of articles of commerce.

Gums Related to Rubber. There are other vegetable latices that yield gums resembling rubber to a certain extent, and that have some uses to which rubber cannot be put. *Gutta-percha* contains more resin than a good grade of crude rubber; it is quite plastic and quite inelastic at higher temperatures and harder at lower temperatures. It finds use in mending tissues, cable insulation, and in fabricating certain surgical supplies. *Balata* is quite elastic and soft when warm, and leathery and only slightly elastic when cold. The resins are largely removed from balata with solvents before it is used. Belting, packing for steam cylinders, gaskets of various sorts, and covers for golf balls employ considerable amounts of balata. Neither of these gums is ordinarily vulcanized. *Chicle*, used in making chewing gum, is a resilient substance exuding as a latex from a tropical tree.

Reclaimed Rubber. It is possible by disintegration methods involving both mechanical and chemical action to obtain from worn and discarded compounded and vulcanized rubber articles a material called "reclaimed rubber." It is in no sense a substitute for rubber, but has certain definite uses in rubber compounding, which make it a valuable material. Obviously the price of crude rubber governs the extent to which this material is used, but regardless of price conditions there is always a definite use for it, since it confers certain valuable properties in compounding, and also aids in mixing and calendering rubber stocks. The fabric, saponifiable material, and soluble mineral matter of shredded waste rubber are dissolved by caustic soda solution under steam pressure and are removed along with free sulfur. Combined sulfur and some mineral matter remain. Ebonite, or rubber vulcanized with a large amount of sulfur, is merely ground and used without chemical treatment in the same way that a pigment or filler is added to a mixture. In 1929 some 230,000 tons of reclaimed rubber were produced in this country, and 14,000 tons were exported.

Making Rubber Compounds. Rubber is a necessary ingredient in the manufacture of a large number of articles of commerce, but practically none of these are made of rubber alone. The rubber industry employs several classes of substances, each class having a definite function. The classes of substances used in compounding may be summarized as follows: reinforcing agents; softeners; colored pigments; vulcanizing agents; vulcanization catalysts (accelerators); antioxidants.

The most commonly used tougheners or reinforcing materials are

carbon black, zinc oxide, clay, lithopone, and whiting. The amounts of these materials depend on the uses of the finished products.

Softeners include heavy mineral oils, petroleum jelly, asphaltums of various melting points, together with some rosin, rosin oil, and palm oil, and for black stocks pine tar, stearic acid pitch, and coal tar. Vegetable oils treated with sulfur or sulfur chloride have some use in the rubber industry.

Colors are inorganic pigments and "lakes" of organic dyes. White stocks result from the use of such white pigments as zinc oxide, titanium dioxide (titanox), and lithopone. It is obvious that lead pigments cannot be used except in black rubber, on account of the formation of black lead sulfide from the sulfur of the compound. Red is a very common shade of rubber, and is obtained by the use of ferric oxide, lakes and crimson antimony sulfide. It is possible to get very vivid and permanent colors in rubber, the demand for light colors being largely for bathing caps, rubber aprons, beach shoes, and toy balloons.

Vulcanizing agents are confined almost exclusively to sulfur and sulfur chloride. Sulfur is mixed with the rubber and other ingredients. Soft rubbers may contain from 0.5 to 5% sulfur, whereas hard rubber requires from 25% to 32% combined sulfur. Sulfur chloride is used only with thin rubber, and is applied as a vapor or in a solution of some organic solvent.

A very large number of chemical compounds, both inorganic and organic, are used as vulcanization catalysts, or accelerators. Lime, litharge, magnesium oxide, white lead, and zinc oxide are the most important mineral substances, and a great variety of organic compounds are used for this purpose. Most organic accelerators contain either sulfur or nitrogen, often both elements being found in the same compound. The general classes in their approximate order of importance include mainly mercaptothiazoles, guanidines, aldehyde amines, thiuram sulfides, and thioureas. Nitrosamines, xanthogenates, thiocarbonates, trithiocarbonates, and heterocyclic bases are also used. Hexamethylenetetramine was formerly used in enormous quantities, but its use is rapidly diminishing.

Antioxidants are materials that will hinder atmospheric oxidation of the finished product. They are mainly secondary aromatic amines, such as substituted naphthylamines, for example phenyl-beta-naphthylamine and the corresponding alpha compound, and others of high molecular weight. Ketene anils have also recently found application.

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Mixing. The ingredients which enter into a rubber compound are proportioned on the basis of 100 parts of rubber, and are weighed, and assembled in containers. When slightly warm and under great mechanical stress, rubber behaves like a very viscous liquid. The oils and tars mix relatively easily, but it requires considerable time and the expenditure of much mechanical energy to get the solid ingredients of a compound properly distributed in the rubber. A great deal of heat is developed in mixing, and this must be removed by flowing water through hollow portions of the mixing equipment. It is necessary of course to keep the temperature below the point at which vulcanization begins, or otherwise incipient vulcanization or "scorching" will occur. If very active accelerators are used, sulfur is added last, final mixing is rapid, and the thoroughly compounded mass is immediately got into thin sheets to insure cooling. It is common practice to work the rubber on rolls or in mixers until it is warm and smoothly plastic before the addition of any other ingredients, this process being known as "breaking down."

Until recent years the open-type two-roll mixer was used exclusively in the rubber industry. Large closed mixers, which operate automatically, are coming into very general use. They eliminate very largely the personal equation, have capacity for handling larger batches, and are also much safer machines to operate.

What is often spoken of as rubber cement is essentially a colloidal solution of rubber and other ingredients in organic solvents such as gasoline, benzene, and carbon tetrachloride. These are made by placing the solvents, rubber, and other substances either in a standard type of closed mixer or in a closed drum, and rotating it until the mixture is homogeneous.

Forming and Shaping Processes. In the manufacture of many products, operations are so timed that the hot material from the mixing rolls or mixers is carried directly over to other machines for the forming of the desired article. It would be out of place in a text of this sort to attempt a detailed description of all the ways in which rubber compounds are gotten into the form in which they are ready for vulcanization. The general principle in all operations is very much the same, namely, to get the rubber into what is to be its final form and then vulcanize, or to place the necessary amount of compound in a mold and by heat and pressure mold it into form and vulcanize it at the same time.

Among some of the methods, these are the most common. Tubing, including auto inner tubes and hose, are made by extruding rubber

from a die under pressure, either directly or around a fabric tube. Hot water bags are made by placing the correct amount of rubber in a mold in which there is a plate, and by heat and pressure causing the soft rubber on each side of the plate to flow around and fill the mold, leaving the end of the bag open. The plate is withdrawn and the bag closed by means of a strip of rubber, which is subsequently vulcanized. Rubber balls may be made by placing two shallow cups in each mold, sealing them together by heat, and, by means of nitrogen from ammonium nitrite, inflating during molding, and vulcanization. Some hard rubber articles are made by placing a plastic compound in a metal mold and heating under pressure to secure vulcanization. The rubber flows out of the cracks in the mold, the excess is broken off or ground

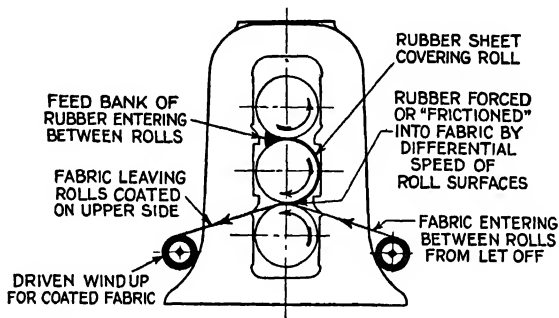


FIG. 120.—Friction Calender. Courtesy Farrel-Birmingham Company, Ansonia, Conn.

off, and the articles are polished on buffing wheels. Combs are cast solid, and the openings between the teeth are sawed out on automatic machines. Thin rubber gloves are made by dipping porcelain "hands" in rubber cement or compounded latex, inverting them, and allowing the solvent to evaporate, the process being repeated until the desired thickness is attained. Gloves of this type are commonly "cold cured."

A great many articles which contain rubber are made by building up layers of sheet rubber and reinforcing fabric, and then by heat and pressure uniting all layers, the rubber being vulcanized at the same time. This involves forming the rubber into sheets of the desired thickness, and cutting these sheets into the proper size and form. It is also often necessary to coat a fabric with rubber in such a way that the rubber is thoroughly worked in between and around the yarn or strands. The most common method of making a sheet of rubber or of coating fabric with rubber is by means of the calender. This machine

consists of a series of superimposed rolls, sometimes four but more often three in number, the axes of which are in the same vertical plane. The rubber compound is fed between the upper roll and the one next below it, passes around this next lower roll, and is taken off between the bottom roll and the one next above it. When fabric is being coated, it is drawn between the lowest and next to lowest roll, and by virtue of a slight difference in speed between the rolls, the rubber is forced into the fabric. This process is known as "frictioning." Calen-

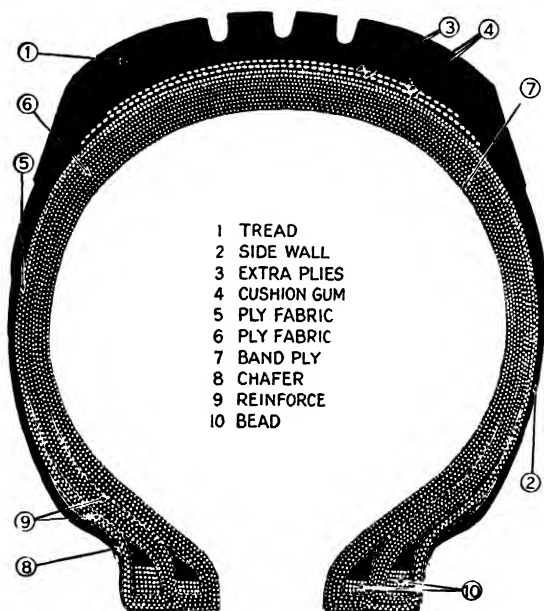


FIG. 121.—Cross Section of Automobile Tire. Courtesy The Firestone Tire and Rubber Company, Akron, Ohio.

ders running on sheet rubber have all rolls traveling at the same speed.

The making of articles from sheets of rubber may be best illustrated by the fabrication of footwear and automobile tires. A rubber shoe is made by cutting from sheet rubber and rubber-covered fabric the parts of the shoe. The calendered sole has been given its corrugations on a pair of rolls, and the parts of correct size cut from this sheet. All trimmings of sheet rubber are run again through mixers and calenders; fabric scrap is ground and used as a filler for such parts as sub-soles. The shoe is assembled, usually by hand on a last, a few

parts of the operation being advantageously accomplished by machines. The shoe on its last is sent to the vulcanizers.

An automobile tire casing is now largely assembled by machinery. The reinforcing fibers in a casing are of cotton, and are a series of parallel cords held together at intervals by weak cross threads or by the rubber with which the cords have been coated. Rubber that coats the fabric is applied by calendering, by impregnating with rubber cement, or by treatment with latex. In order that a tire may be firmly

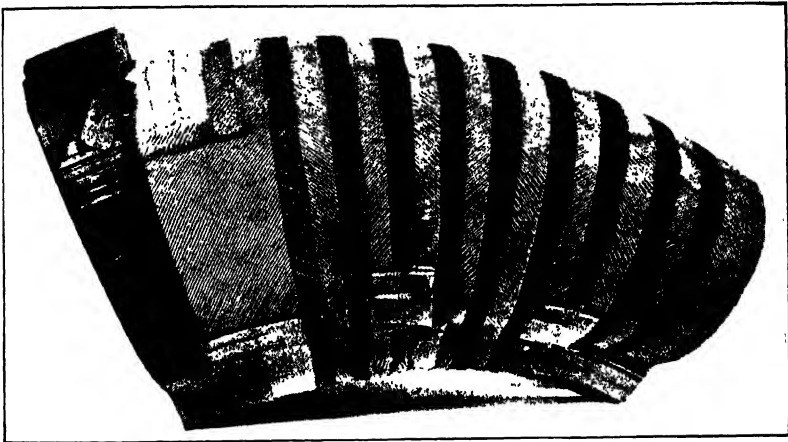


FIG. 122.—Section of Automobile Tire (layers cut away to show structure).
Courtesy The Firestone Tire and Rubber Company, Akron, Ohio.

attached to a wheel of a vehicle, the common practice is to provide in the tire two loops, called "beads," which are prevented from stretching by means of steel wire imbedded in rubber. After the beads and fabric are assembled, the side walls are applied. The purpose of these is mainly to protect the fabric against moisture. This portion of the tire suffers relatively little wear except through scraping curbs or running in deep ruts. A strip of soft rubber, which functions as a cushion, is laid peripherally and covered with a thickness of special fabric, and on this is laid the tread, which is compounded to give the maximum of wearing qualities and resistance to abrasion. Both zinc oxide and gas black in varying proportions are used in making tread stocks. Tests with a sand blast show that a good grade of tread rubber will stand wear four times as well as tool steel. When the tire has been assembled, its component parts are held together sufficiently well by the tackiness of uncured rubber to permit ordinary handling. After

the process of vulcanization, the parts are so welded together that the tire becomes a unit, and it is easier to tear the actual rubber and fabric than it is to separate one part from another.

✓**Vulcanization.** In the manufacture of all articles containing rubber, it is necessary to change the physical properties of the rubber by means of sulfur or sulfur chloride so that the temperature range through which it retains its desired properties, neither becoming brittle nor sticky, may be sufficiently extended to meet conditions of use. The process also renders the product less soluble in organic solvents, more water-proof, and generally more durable. Since sulfur chloride (cold vulcanization) is limited in its use to thin sheets of rubber, attention will be centered primarily on hot vulcanization by means of sulfur. This process usually involves heat, and in the making of many articles pressure is employed as well.

Just what takes place in the process of vulcanization of rubber by means of sulfur is still by no means clearly understood. Colloid chemists explain vulcanization as an adsorption phenomenon. The purely chemical point of view is admirably summed up by Fisher in Chemical Reviews (March 1930) in these words:

The evidence for the chemical combination with sulfur is chiefly as follows: that when extracted with a liquid which dissolves sulfur but not rubber (for example, acetone) the sulfur is not removed beyond a certain definite amount, this amount depending on the conditions under which the rubber was vulcanized; that when so extracted with acetone to remove the free sulfur, and then extracted with hot benzene, each fraction, dissolved and undissolved, contains the same proportion of combined sulfur as any other fraction and as the original; that there is no measurable transfer of sulfur when vulcanized rubber is heated with some raw rubber in solution; that when raw rubber is heated in solution with as much as 1000 per cent excess of sulfur, the product contains no more combined sulfur than the amount required for saturation of the rubber hydrocarbon as determined by other means, both chemical and physical; that the amount of unsaturation of vulcanized rubber, as determined by the addition of bromine and iodine chloride, corresponds to the difference between that which can be accounted for by the combined sulfur using one atomic equivalent of sulfur for each C_2H_4 group, and the unsaturation of the original rubber; and that the rate of chemical combination is regular, and the velocity coefficient of the reaction has been found to be 2.65 for 10 degrees' increase in temperature, a value agreeing with that generally obtained in the case of a chemical reaction. The combined sulfur has never been removed from vulcanized rubber and the original rubber regenerated. In other words, rubber has never been completely devulcanized. Furthermore, completely saturated rubber, hydorrubber, is not affected by treatment

with sulfur chloride. These facts leave no doubt that sulfur combines chemically with the rubber hydrocarbon, and they help to show that the theory of adsorption is untenable.

Fisher reviews the various explanations of the action of sulfur, and concludes with this sentence:

The question is quite open, and further work must be done to find out whether vulcanization is chiefly a polymerization, whether the method of combination of the sulfur causes the change, or whether the change is due to reaggregation, the dispersion of sulfur addition products, etc.

Vulcanization accelerators have the two desirable effects of lessening the time and lowering the temperature of vulcanization. The time effect is particularly important since in some articles, as for example automobile tire casings, there are several different compounds in the side walls, tread, and cushion, which must be cured at the same rate and finished at the same time. By the use of different accelerators this result may be accomplished. The most common explanation of the way in which accelerators act is that they cause the formation of a more active form of sulfur.

The vulcanization with sulfur involves heat, and for most articles pressure is also necessary. Dry heat at atmospheric pressure is used with light-colored goods compounded with very active vulcanizing accelerators. Articles which are fully shaped and which retain their shape during vulcanization may be wrapped with wet cloth and subjected to the action of steam under pressure. Those articles which take their final shape by means of pressure applied to molds are vulcanized by heat supplied to hollow portions of the press, or by a combination of pressure and steam surrounding the molds, which are in a closed chamber or autoclave. Automobile tire casings are vulcanized in individual molds, which are known as the "watch case" type of vulcanizer. Steam at 40 lb. to 60 lb. pressure is used. Within each tire ordinarily is a heavy rubber bag containing water, and the steam pressure against this bag forces the rubber against the inside of the mold.

The cold process, applied to thin-walled articles, involves the use of sulfur chloride, either as a vapor, or in solution in benzene, carbon tetrachloride, or carbon bisulfide. Excess sulfur chloride is decomposed and removed by ammonia gas.

Uses of Rubber. The uses of articles or materials of which rubber is the chief component are so varied as to defy enumeration. Prac-

tically every field of human activity includes at some point something or many things made of rubber. Those uses which are the most obvious and common are these.

Automobile Tires. Even very large trucks are now generally equipped with pneumatic tires, since the solid type of tire is very rapidly going out of use. Most engine- or motor-driven vehicles which

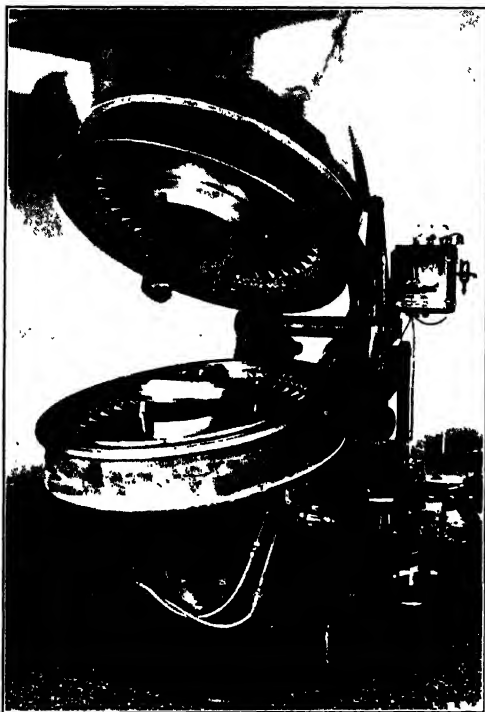


FIG. 123.—“Watch Case” Tire Vulcanizer. Courtesy American Society^{*} of Testing Materials.

run on roads use pneumatic tires composed of an outer casing within which is an inflated tube. Bicycle tires are ordinarily single inflated rubber and fabric tubes.

Footwear. The uses of rubber in footwear extend from heels and soles of ordinary leather and canvas shoes through all sorts of overshoes and arctics to boots of every variety.

Clothing. Damp-proofed or water-proofed clothing in which rubber has a part is usually made of a fabric which has been coated with rubber or of two layers of fabric between which is laid a sheet of rubber. Although rubber gloves are usually classed as "druggists' sundries," the heavier varieties may be considered as protective clothing for electrical workers and those who handle acids and other corrosive chemicals.

Insulation. Copper or aluminum wire that has to come in contact with other materials is commonly insulated by coating it with a rubber compound, which may in turn be sheathed with fabric or lead.

Hard Rubber. Storage-battery cases, switchboards, and other electrical equipment, and pipes and containers in chemical plants, are often made of hard rubber, although synthetic plastics have invaded this field to a considerable extent.

Hose. Fabric woven into a tube and coated with rubber either on one or both sides is used to convey fluids, both gases and liquids, and even, in the compressed-air method, powders and coarsely ground materials. Fire hose and air hose must stand high pressures, and hose used for making flexible connections between locomotives and their tanks and the cars which they pull must withstand both heat and pressure. The rubber tubing and connections of the laboratory constitute a considerable use of rubber.

Belting. The wearing qualities of rubber are taken advantage of in coating belting both for power and for conveying solids. Not only ordinary powders and crystals but such abrasive materials as ore, coal, coke, and lump rock are carried on rubber-covered belts.

Packing. All sorts of packing, washers, and gaskets contain rubber along with cotton fabric, asbestos, and wire. A writer on the subject of rubber has said, "Of all the applications of rubber, that of packing for the steam engine and connecting machinery appears to have been the most important, as it has been an essential condition of the development and extended use of steam as a motive power." Although the pneumatic tire may be regarded as having an equal claim as a factor in modern civilization, the packing of the power plant engine or the locomotive should not be overlooked.

Sporting Goods. Modern sport depends very largely on rubber. Footballs, basket balls, tennis balls, polo balls, and the like, are inflated and retain their form and resiliency because of impervious rubber. Baseballs have a rubber core, and golf balls are made of rubber threads wound with tension on a solid or plastic core and covered with a rubber and balata compound.

Druggists' Sundries. The term "druggists' sundries" includes a wide variety of household and hospital supplies such as sheet rubber, hot water bags, ice bags, combs and other hard rubber articles, surgeons' gloves, bathing caps, and toys such as balls, dolls, and balloons. Hospitals would be helpless without rubber, and many of the conveniences of the home depend on it.

CHAPTER XXIV

COAL PRODUCTS

All industries connected with the products of coal may be divided into the major section of those that make fuel and the minor section of those that handle by-products. There is so much in chemical literature, and also in what is read by those untrained in chemistry, concerning the by-products of coal that the true perspective is often lost. These facts should be borne in mind. Not more than 15% of all coal mined is subjected to any treatment that involves chemical change other than combustion. The main by-product of carbonization of coal, which is tar, is either burned as such or worked up into roofing and road tars. A very small fraction of the total weight of the coal appears in all the light oils, ammonia, and minor by-products combined. These by-products are very useful, but coal is not subjected to any sort of process whose primary purpose is to obtain these substances. The three main objectives of "processing" coal are to make coke and coal gas, water gas, and producer gas. Both water gas and producer gas are largely made from coke, resulting from making coal gas, but both can be made from coal.

COAL GAS AND COKE

The fundamental idea behind coal carbonization is to heat bituminous coal of a certain type at a high temperature until the coal is converted to coke in a retort or oven from which gas may escape but to which air does not have access. The first coal gas was made by Murdock in London early in the nineteenth century. Fireclay retorts have been in use since the early years of the coal gas industry, supplanting the earliest iron retorts. The modern by-product coke oven holding a dozen tons or more at a single charge was developed by the steel industry, and is now rapidly taking the place of the smaller retort. Coal gas in the earlier years of the industry was used almost entirely as an illuminant. The coke made in the small retort was of little value in a blast furnace, and metallurgical coke was made with-

out any effort to recover the gas or the ordinary by-products of coal carbonization. With the development of electric lighting, coal gas gradually lost ground as an illuminant. At the same time its use as a domestic and industrial fuel has increased. The decrease in the demand for illuminating gas and the lowering of heating value requirements opened the way for a more extended use of blue gas, and made possible the growth of the by-product coke-oven method of coal carbonization. A modern coke oven not only makes a satisfactory grade of metallurgical coke, but also produces a gas that meets municipal standards, and this with the recovery of all by-products. There is thus a very decided trend on the part of the coal gas industry to one type of carbonization, the by-product coke-oven method.

Until recent years the only temperature at which coal was carbonized was around 1000°C ., but within the past few years a great deal of experimental and development work has been done on processes in which the temperature is from 600°C . to 700°C ., and which give very different amounts and kinds of coke, gas, tar, and by-products. For this reason, the distinction is made in the coal gas industry between "high-temperature carbonization" and "low-temperature carbonization." The former continues to be the type almost exclusively used, while the latter has made little progress.

Not all bituminous coal makes satisfactory coke. There are "non-caking" coals which, when heated to 1000°C . in the absence of air, leave a residue resembling the original coal in appearance. A "caking" coal, on the other hand, fuses and swells, and when all gas has escaped, the cooled residue is a hard, porous, lustrous, grayish black mass. This property of caking has little or no relation to the quantity of "volatile matter." Caking seems to be due to components in the coal that melt when heated and serve as binding material. Slow heating destroys this caking property. Although on a large scale the process of distillation appears slow, the effect is really one of rapid heating, the actual amount heated at one time being comparatively small. Spongy coke is the result of excess binding material. The plastic range of caking coal has been studied by passing gas through the coal and plotting the rate of gas flow against temperature, the rise of temperature being uniform. The ultimate standard on which coals are selected for carbonization is the kind of coke they make.

It is frequently found desirable to mix low-volatile and high-volatile coals. Mixing for reduction of excess binding material is common practice. The primary object of mixing is to produce the desired coke structure from available coals. Some coals, notably a number

from Illinois and Indiana, produce no "sponge," but are usually mixed with low-volatile coal to improve the coke structure. An expanding coal must be mixed with a shrinking coal to avoid extraction troubles and danger of injury to the oven walls. In making blast-furnace coke, the prevailing practice is to use 15% to 20% low-volatile coal and the remainder high-volatile; in making domestic and water-gas coke, mixtures with 20% to 30% low-volatile coal are often employed; and in making foundry coke, the percentage of low-volatile may be even higher. Typical high-volatile coals run between 32% and 38% volatile matter. The size to which the coal is reduced is also an important factor in the nature and quality of the coke.

Several different types of materials have been isolated in microscopical examination of coal, none of which are simple chemical substances. Little is yet really known of the chemical changes that take place during the pyrolysis of coal. The physical changes include fusion to a mass of the consistency of pitch, an evolution of vapors from the fused material, and finally the formation of a porous solid. When the coal is introduced into the red-hot oven, that portion next to the walls fuses, while the bulk of the charge is much cooler. The fused layer on each side is resistant to the flow of gas. As coking takes place the two fused zones, which are quite thin, approach each other at the rate of a little more than one inch per hour, and between each fused zone and the wall of the oven is a mass of red-hot coke. Within the fused layers is unchanged coal into which relatively little heat penetrates. Vapors bubble through the fused material, giving it a porous, cellular structure, and escape through the red-hot coke. Ultimately the two fused layers meet, and the contents of the retort consist of a slab of coke divided down the center by a very distinct crack, which marks the place of meeting of the two fused layers, and in addition has irregular horizontal fissures.

Carbonization takes place practically at atmospheric pressure. There are inevitable leaks from cracks in retorts and ovens as well as around doors. If pressure develops to an appreciable degree in the retort or oven there will be loss of volatile carbonization products, whereas a slight suction means admission of furnace gases and air. Hence pressures are very carefully regulated, a delicate balance is maintained, and there is practically no loss of gas or dilution by air and furnace gases.

Two types of thermal decomposition may be recognized in high-temperature carbonization. The first is represented by the fusion of the coal and evolution of vapors as the result of a series of slightly

exothermic reactions. The higher the oxygen content of the coal compounds, the greater is the amount of heat developed. It is quite probable that the six-membered rings found in some products of distillation were already present in the original coal. The primary products are known to be saturated hydrocarbons, both naphthenes and paraffins, with smaller amounts of olefines and a considerable amount of higher phenols. The products pass over red-hot coke, and over the inner surface of the heated oven walls until they escape from the oven. In their passage the fixed gases are relatively unaffected, but those substances that are liquids at room temperature, and especially those of low vapor pressure, are profoundly affected by the high temperature and the catalytic effect of the porous surface of the coke. Hydrogen is lost from saturated compounds to form unsaturated compounds. Side chains break away to form simple hydrocarbons, leaving unsubstituted or less completely substituted six-membered rings, which ultimately attain the type of unsaturation represented by benzene and its homologues. At the same time, hydrogen is replacing hydroxyl, and in turn the hydrogen is continually removed with the formation of aromatic hydrocarbons, so that only a small amount of the lower phenols is left. The reactions are evidently mainly pyrolysis reactions, and there is relatively little pyrogenesis of hydrocarbons, a view contrary to the older idea that benzene was largely the result of the polymerization of acetylene.

The use of a number of retorts and ovens and maintaining a definite schedule of filling them with coal and removing coke from them may be referred to as "staggering" of charges. At any one time there are different conditions of progress of distillation in each retort. The gas from the carbonization units is mixed in the holders, which contain from one-fourth to one-sixth of a day's demand. The gas delivered from a coal-gas plant is thus practically uniform in composition. If a single oven or retort is considered, the product varies very considerably as carbonization progresses. With each successive hour the yield, illuminating power, heating value, and percentage of hydrocarbons diminish, while the percentage of hydrogen continually increases. Tar and ammonia reach a maximum value and then decrease. The effect of temperature on yields of various products is taken into consideration, and a temperature is maintained that gives the greatest value for the energy consumed. The higher the temperature the greater the total yield of gas in cubic feet. The heating value of the gas in B.t.u. per cubic foot increases with temperature to a maximum, after which it decreases.

Coal-gas plants may be considered as falling into one or the other of two classes, those which use retorts and those which use ovens. As late as 1910 it would have been correct to say that the two classes were city gas plants and by-product coke-oven plants. Now the newer and more up-to-date city gas plants are installing coke ovens, and as the older plants wear out, they will probably be replaced with ovens. Fully ten times as much coal is carbonized in coke ovens as in retorts, and this proportion will likely continue to change still more in favor of coke ovens. However, present conditions are now being discussed, and all types will be described.

A retort is ordinarily a fireclay tube, made up of a number of curved shapes, with iron doors at both ends, which holds a relatively small charge of coal; an oven is built up of silica brick and is a long, deep, narrow chamber holding several tons of coal. The older retorts were known as "stop end" with one end closed and the other with a door, but most are now "through" retorts with doors at both ends. Some of the newer vertical retorts are much larger than the ordinary retort, and are really small ovens set on end. There are three classes of retorts, horizontal, inclined, and vertical. Most of the older city gas plants in the United States are equipped with the horizontal type; there are only a few plants using inclined retorts; and a number of more modern plants use vertical retorts. Most horizontal retorts are D shaped and are about 20 ft. long, some 16 in. high, and 26 in. wide, the last two being inside dimensions. They are set with the flat side down, and are arranged in groups known as "benches," each bench having a single producer to generate the gas used in heating its retorts and one or two combustion chambers communicating with flues around the retorts. Typical benches are made up of three horizontal rows of retorts with two or three retorts per row. The retorts are equipped with iron doors, which are hinged and sealed during a run by mud made from clay and water. All retorts in a row of benches are charged at the same end and discharged from the opposite end. The gas is taken off from either one or both ends of the retort, being carried up to the top of the bench and into a common main, the discharge pipe from each retort dipping under the surface of liquid to serve as a seal to prevent entrance of air. Horizontal retorts are charged by rams, sectional scoops, or by a variable-speed belt that throws the coal into the retort. In the last system of charging, the speed of the belt is governed by the weight of the charge remaining in the feed hopper. When a retort is charged, the door on the charging end is locked in place. The retorts are maintained continually at a high

temperature. An ordinary "through" retort will hold about 1000 lbs. of coal, and the carbonization time is of the order of 8 hours. At the end of the operation the doors are taken off and a ram is pushed through the entire length of the retort. The charging and pushing equipment are together on a truck which runs on a wide track along a row of benches. The hot coke drops on a steel conveyor and is quenched by water sprays. A part of it is pushed directly into the producers, which are built in at the base of each bench.

Inclined retorts are ordinarily of oval cross section and are set at an angle of about 30 degrees. The charge is of the same order of magnitude as that of a horizontal retort. Gas is taken off at the lower or discharge end. At this end is a casting that prevents the charge from sliding down against the lower door. The retorts are charged by pouring in the coal from a hopper at the upper end. At the close of a run the door and stop are removed and the charge slides out with the assistance of a poker, drops on a horizontal conveyor, and is sprayed with water to quench it.

Vertical retorts are either continuous or intermittent in their operation. Vertical continuous retorts are always practically fully charged. Coal is either put in at frequent intervals to take the place of coke removed at the bottom at about the same rate, or the feed and discharge may be entirely continuous. The coal thus gradually slides down the retort, is carbonized, and the coke cools considerably as it passes out of the heating zone and moves to the discharge valve at the bottom of the retort. Intermittent vertical retorts are operated in essentially the same way as horizontal retorts except that their charge and discharge are by gravity. Some vertical ovens are oval in cross section, but the larger ones are rectangular, so that the coal and coke form a fairly thin, wide slab. They may hold as much as four tons of coal, and are thus in reality small-sized ovens.

Both inclined and vertical retorts are heated by producer gas. Some producers are of the stationary, built-in type. With the exception of a few regenerative installations the primary and secondary air in American plants are preheated in recuperators. More modern plants use separate outside producers and have waste heat boilers after the recuperators.

A modern by-product coke-oven plant consists of one or more batteries of ovens, the larger plants having fifty or more ovens to the battery. The oven itself is a long, deep, narrow chamber of silica brick. Typical lengths are of the order of 40 ft., the depth is 10 to 15 ft., and the width from 14 to 20 in. Many ovens of this type used

for supplying cities are much smaller than this. The oven is slightly wider at one end than the other to facilitate discharge. At each end are removable iron doors. Each oven of one type has its own separate system of heating flues, but in most cases each row of heating flues serves to heat two ovens. The flues may be horizontal and connected so that all the preheated air is fed into the first flue and successive amounts of gas are introduced as the gases change direction in passing from one flue to the next. By alternately beginning at the top and bottom on each side, the whole oven may be kept at a reason-

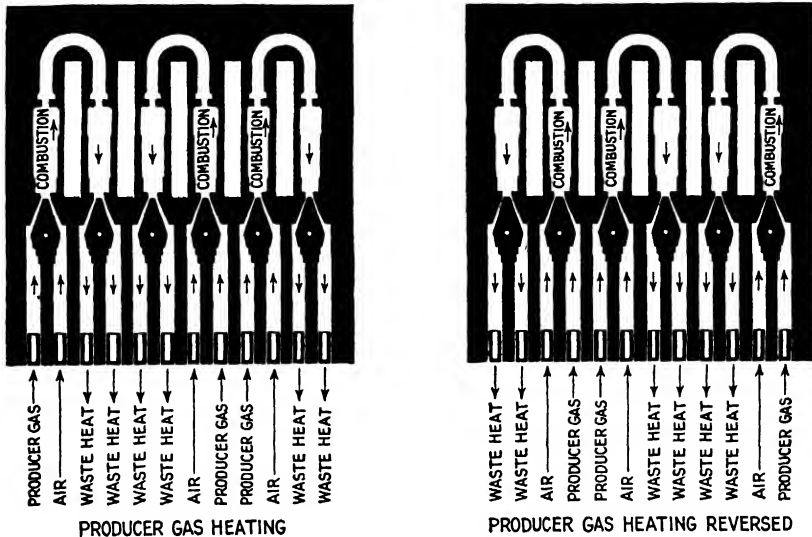


FIG. 124.—System of Flues and Regenerators, Koppers By-Product Coke Ovens.
Courtesy The Koppers Construction Company, Pittsburgh, Pa.

ably uniform temperature. The arrangement in one very widely used type of coke oven is a series of vertical flues in which gas is mixed with air and in which combustion takes place. The products of combustion enter a horizontal flue and pass from it by "cross-over" flues to the opposite side of the oven into another horizontal flue. From this they are distributed into series of vertical flues and pass down through these to the regenerator chambers with which each set of vertical flues is provided. By dividing the horizontal flues with partitions and supplying several cross-over flues, the space occupied by the horizontal flues is small and the setting has greater mechanical strength. By reversing the direction of combustion sufficiently often in each series

the oven temperature is constant enough to insure the efficiency of the operation.

Coke ovens are charged through holes in their tops. A series of hoppers set into a wide truck frame which runs on rails about 30 ft. apart constitutes what is known as a "larry car" and carries the charge to each retort. In some recently built plants, charging is done into a single hole in the top of the oven with a single hopper larry car, and in these two collecting mains are provided, one at each end of the oven to take care of the rush of gas from fresh coal. A small amount of air is drawn in during the charging by means of steam jets in the

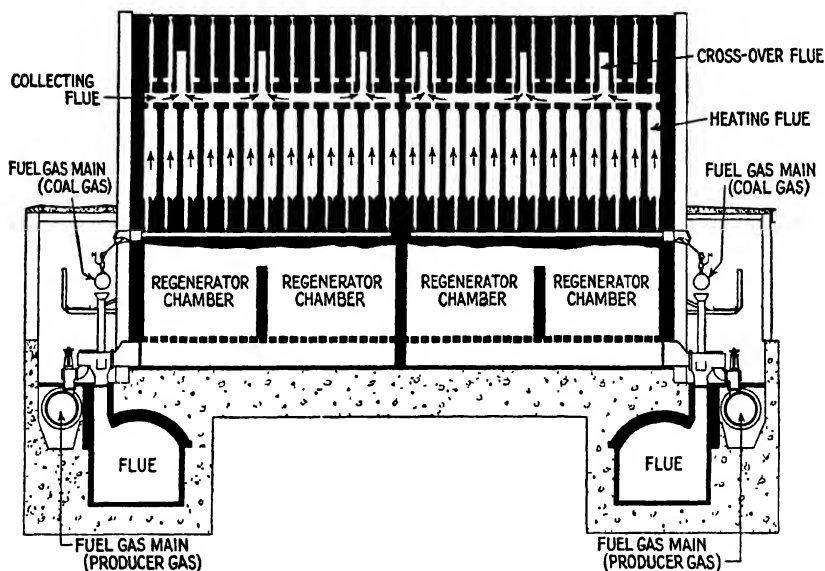


FIG. 125.—Cross Section of Flues and Regenerators, Koppers By-product Coke Ovens. Courtesy The Koppers Construction Company, Pittsburgh, Pa.

offtake pipe, the purpose being to prevent escape of gas with consequent smoke and flame. After leveling the coal by a bar, all charging openings are sealed, the doors having been wedged on and sealed before charging began. Several recently built plants are equipped with "self-sealing" doors, which eliminate the use of "mud." The time required varies with the size and type of oven, but is seldom less than 12 hours and is more commonly of the order of 18 hours. At the end of this time the oven contents are a mass of red-hot coke. Both doors are taken off, and a girder with a plate on its end slightly smaller than the smallest cross section of the oven is pushed from the small to the

large end of the oven. As the pusher moves through, a steel car moves forward at the opposite end of the oven, and catches the blazing lumps of coke as they pass through slatted guides, break from the main mass, and fall into the car. By the time the oven is clear the car has moved up until it is evenly filled through its entire length. The car is run to the end of the line of ovens, and water is poured on it from an overhead tank at such a rate that the burning coke is quenched in a few seconds. Some progress is being made in saving the larger part of the heat of the coke in a "dry quenching" process in which cold waste gases composed mainly of nitrogen with some carbon

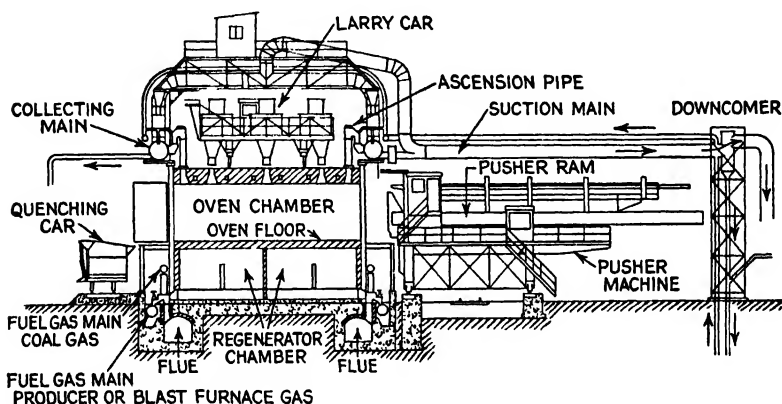


Fig. 126.—By-Product Coke Oven. Courtesy The Koppers Construction Company, Pittsburgh, Pa.

dioxide are passed through the coke, remove the larger part of the heat from the coke, and go to waste heat boilers and dust catchers before recirculation. The quenching chambers are made of steel lined with firebrick. Hot coke is fed into the top and is reduced in temperature to about 600° F. before it is discharged from the bottom. Since some gas is produced by distillation of "green ends" from the ovens, air is admitted to furnish oxygen to burn the gas. This process is also said to give a somewhat more uniform grade of coke free from fines.

The gas made in the ovens is often used for fuel to heat these ovens, so that 40% of the total output finds use in this way. There is a continually increasing tendency to locate coke-oven plants so that all the gas may be used or sold where high-quality gas is needed, and to heat the ovens by burning producer gas. When this is the policy of the plant, the producers are usually separate and of the

modern type in which feed, stirring, and ash removal are continuous. A few coke-oven plants at steel mills use blast-furnace gas. Producer gas and the air with which it is burned must be preheated, and in

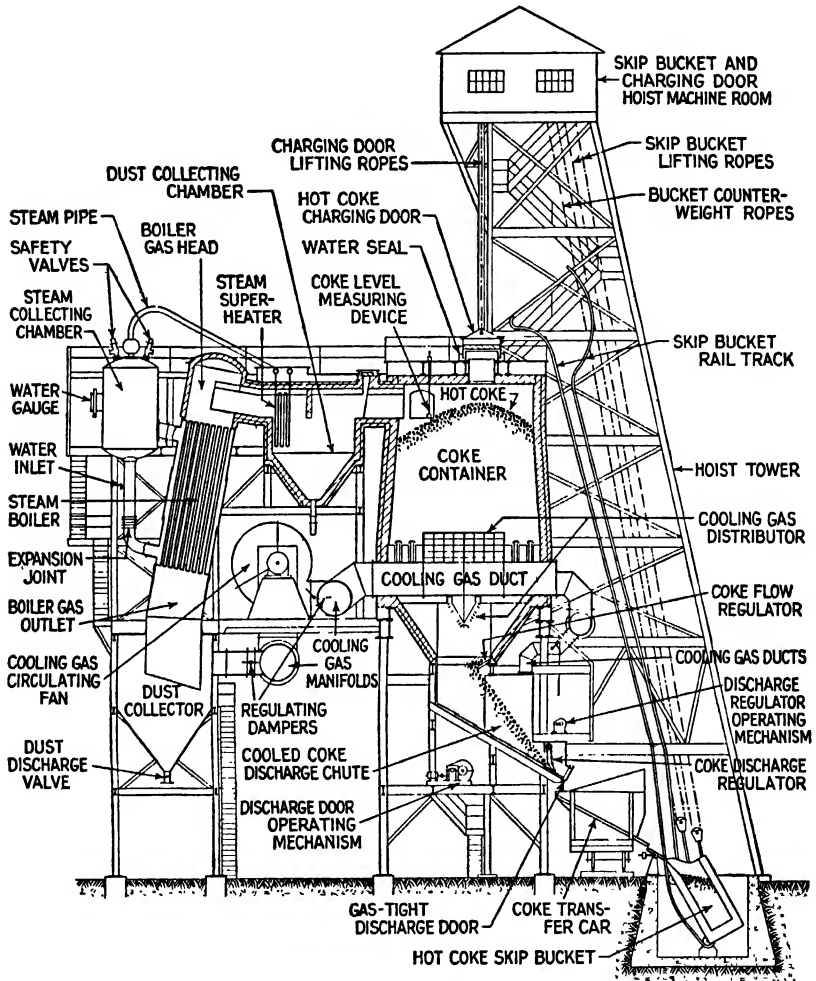


FIG. 127.—Coke Dry-Quenching System. Courtesy Lancaster Iron Works, New York City.

most by-product coke-oven plants the regenerative system is used. Each oven has its own individual set of regenerators. Intervals of about 30 minutes represent standard practice. When producer gas is burned, it enters through one regenerator and air through another;

but when coke-oven gas is used, it is not preheated, and air enters through both regenerators. In both cases the waste gases escape through both generators. The waste gases from each regenerator pass into a horizontal flue that runs under the battery for its entire length.

The two main products of coal carbonization are coke and gas. All by-products, with the exception of a little carbon which collects in the exit pipes from retorts and ovens, are removed from the gas in a series of purification operations.

Coking in Beehive Ovens. Some coke is still made in the beehive type of oven, in which all gas and by-products are wasted. Before the development of markets for gas and by-products the beehive oven was in very general use. Its sole object was to make coke for use in pig-iron blast furnaces. Because the demand for gas and those substances recoverable from it is reasonably steady, whereas the demand for coke is seasonal and irregular, and because by-product coke ovens must be kept continuously hot and in operation whereas beehive ovens can be run intermittently, the beehive oven takes care of peak demands, and is out of commission when regular production levels are reached. Only a small percentage of the total production of coke in the United States is from beehive ovens. A beehive oven is a brick hearth some dozen feet in diameter and seven to eight feet deep, covered with a shallow dome of refractory brick. Assuming the oven to be hot, either from a wood fire or a previous run, coarsely ground coal is charged through a hole in the top until it is about two feet deep over the hearth. The door in the side of the oven is bricked up to within two or three inches of the top. The heat of the hearth starts distillation, the volatile matter that comes off burns, and the heat reflected from the dome continues the carbonization. As the evolution of gas slackens, the opening in the door is restricted. When coke formation is complete, the brick in the door are taken out and the charge is quenched in position to a sufficient extent to prevent its burning when drawn into the air. The old notion that beehive coke is better than oven coke has practically vanished, since experience has shown that any differences are in favor of the oven product.

Coke. This substance is hard and porous, and has a grayish black and somewhat metallic appearance. It averages about 30 lb. per cubic foot. In order to avoid excessive brittleness and low combustibility, it is pushed when slightly "green," that is with about 2% volatile matter still remaining. Only a little of the original ash volatilizes, this loss being largely alkali and iron salts. Most coke contains only a very small amount of phosphorus. About half of the

nitrogen of the coal remains in the coke, and the sulfur is about equally divided between gas and coke. The sulfur of coal appears in coke as sulfur in solid solution in carbon, as sulfur either adsorbed on or loosely combined with carbon, and as metallic sulfides, mainly ferrous sulfide.

The coke, after quenching, is dropped on a sloping wharf of steel plates, where it is examined for unquenched pieces. After final quenching of "hot spots" the gates on the lower side of the wharf are lifted and the coke slides off to a conveyor, being carried to bar, shaking, and revolving screens. The larger sizes are used in the blast furnace; most of the smaller sizes are employed as domestic fuel. All material under one-half inch is called "breeze," and is used as an industrial fuel on chain-grate stokers. Coke is also extensively used in non-ferrous metallurgy, in lime burning, and especially in making water gas and producer gas. The yield of coke varies mainly with the type of coal carbonized. Average yields are around 70% of the weight of the coal, and the heating value is from 11,000 to 13,000 B.t.u. per pound.

Gas. The gas as it comes from the carbonization is a mixture of gases, vapors, and finely divided liquid particles. In the older plants, each pipe from a retort dipped below the liquid level in a U-shaped main called the "hydraulic main." More modern retort plants circulate tar and ammoniacal liquor through the "dip pipe," and provide individual wash boxes, which function like the hydraulic main. Oven plants collect the gas from each oven in a large collecting main through which tar and liquor are sprayed and circulated but in which there is no effort to provide a liquid seal. In all these, there is deposition of one-half to two-thirds of all the tar in the gas, and a considerable part of the water. Naturally the water holds in solution ammonia and ammonium salts. Heavy pitches are removed from the circulating liquids at intervals.

The gas is passed through condensers both to cool it and to facilitate removal of impurities. Condensers are in the main tanks made in two horizontal compartments connected by a series of pipes. Water flows into the lower compartment and rises through these pipes to the upper compartment, from which it overflows. The gas passes around these pipes and gives up the larger part of its heat to the water. The arrangement may be reversed, the gas passing through the pipes and the water in the space around them. Indirect primary coolers usually have several vertical compartments. There are in some cases two sets

of condensers, the primary and the secondary, but in modern by-product coke-oven plants secondary condensers are seldom used.

An exhauster, which is either a low-pressure blower of the fan or double figure 8 type or a high-speed turbo exhauster, serves to move the gas through the system and also functions as a centrifugal and thus removes about three-fourths of the tar that remains in the gas. The pressure developed by these blowers is of the order of 70 to 80 in.

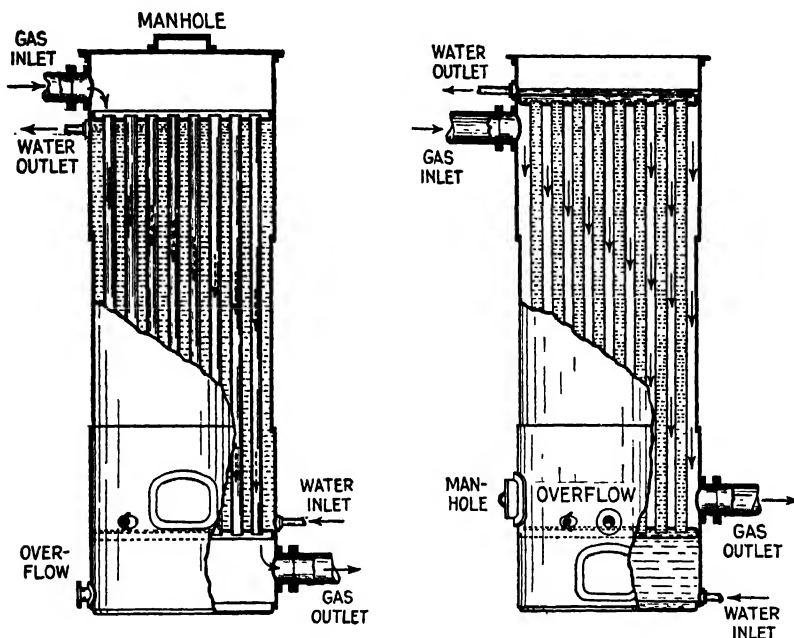


FIG. 128.—Gas Tube and Water Tube Condensers Courtesy The Gas Machinery Company, Cleveland, Ohio.

of water, which is sufficient to force the gas through all the remaining purification system. The location of the exhauster varies, but in most plants it is just before the tar extractors. In some modern by-product coke-oven plants it follows the tar extractor.

Surface condensers are being displaced to an increasing extent by washer coolers in which the gas passes through a spray of ammoniacal liquor, which is cooled by circulating it through water-cooled pipes. Washer-coolers are simple towers provided with wooden grids over which the water flows, dropping from one grid to the one next below it. The gas and washing liquids travel in opposite directions. In all

cooling operations the tar condenses until all that is left is a mist of very small liquid particles surrounded by an adsorbed film of gas.

The standard method of final tar removal is the Pelouze and Audouin tar extractor, known commonly as the "P and A." It consists of a series of concentric bells of rectangular cross section inside a cylinder and dipping into tar. In alternate bells there are small and large holes in great number, but so arranged that a hole in one bell does not coincide with a hole in the bells next to it. The gas is thus subjected to rapid and successive changes in velocity and direction. The bells are counterbalanced so that increasing gas pressure lifts them further out of the tar and exposes more holes through which the increased volume of gas passes. The fine particles impinge upon a surface covered with tar, and are dissolved, while the gas passes on. Electrostatic precipitators are being used with considerable success in removing tar fog from coal gas. The precipitators are of the pipe and wire type. The collected tar flows freely, and no resistance is offered to the passage of the gas. Two precipitators, each working at 95% efficiency, mean practically complete removal.

The gas now contains the vapors of some substances, particularly benzene and its lower homologues, and naphthalene. The partial pressure of these substances in the gas is less than their vapor pressure in equilibrium with their solid or liquid phases, hence they are not removed by ordinary condensation. There are also present in the gas such substances as ammonia, hydrocyanic acid, hydrogen sulfide, and carbon bisulfide.

Ammonia is removed from coal gas by two general methods. One is to scrub all the ammonia from the gas by water and to make from these washings, and from the ammoniacal liquor which separates in the tar settling tanks, such commercial products as aqua ammonia, anhydrous ammonia, and ammonium sulfate. The second method involves removing ammonia from ammoniacal liquor, putting it back into tar-free gas, heating the whole mass of gas with steam, and scrubbing the warm gas with sulfuric acid with continuous removal of ammonium sulfate from the scrubbing acid. The ammonia is removed both for its value and because in burning the gas some oxides of nitrogen would be formed. It is estimated that only about one-fourth the total ammonia content of the gas, both free and combined, is taken out as ammoniacal liquor, and that about three-fourths must be removed, by washing either with water or sulfuric acid. Ammonia washers employing water are operated on the counter-current principle. The water is brought in contact with gas by a number of

methods including flowing down bubbling plate columns, distribution over wooden grids or other packing on towers, by being lifted in thin layers on bundles of rods rotating on a central shaft in a horizontal shell, and by being sprayed either into empty towers or in superimposed compartments in which concentric inverted cones are rapidly rotated.

Coal gas contains a small amount of hydrogen cyanide, HCN, also known as hydrocyanic or prussic acid. It is called "cyanogen" in the gas industry, but it is unlikely that any appreciable amount of cyanogen, C_2N_2 , is actually present. Hydrogen cyanide amounts to about one pound per ton of coal carbonized. On account of its corrosive nature it should be removed from city gas, and most gas companies do this in connection with the removal of hydrogen sulfide. It is inefficiently removed by iron oxide purification and practically completely by liquid purification, but the products are as yet not much used commercially. In the few cases where the removal of hydrogen cyanide is undertaken for commercial purposes, iron salts are commonly employed.

The original nitrogen of the coal is distributed approximately as follows: one-half remains in the coke, somewhat more than one-fourth escapes as nitrogen in the gas, less than one-fifth appears as ammonia and ammonium compounds, and the small amount that remains is mainly in the tar. Only a little over 1% is accounted for in the gas as hydrogen cyanide.

Naphthalene causes no particular trouble in warm weather, but gas carried in exposed pipes in cold weather gradually deposits naphthalene with consequent clogging. Hence it is necessary to scrub it from domestic coal gas by a petroleum distillate in the gas oil range. The amount of naphthalene varies from 10 to 30 grains per 1000 cu. ft. and may be reduced by scrubbing to values varying from 4 grains to less than one grain. Relatively small amounts of oil are necessary and very little light oil is taken from the gas. If a little air is admitted to the system and time is allowed, gum-forming substances of the nature of oxidation products are removed. Water scrubbing for naphthalene removal is mainly a matter of condensation rather than solution. In Europe, creosote oils are employed, the dissolved naphthalene increasing their value as wood preservatives.

The coal gas still contains vapors of benzene and its lower homologues, their partial pressures being less than their equilibrium vapor pressures. These substances have high heating values, and only enough are scrubbed from the gas to meet the demands of synthetic

organic chemical industries. The price of motor fuel made from petroleum is usually too low to make profitable any extensive recovery of light oils for this purpose, in spite of their high anti-knock value. For certain purposes the lower aromatic hydrocarbons are better solvents than aliphatic hydrocarbons from petroleum.

The method universally used to remove light oils from gas is scrubbing with petroleum distillates of low vapor pressure which are efficient to the extent of about 92%. As some of the light oils dissolve, they serve to increase the solvent power of the liquid for the remaining aromatic hydrocarbons. Some progress has been made in absorbing the light oils by means of activated charcoal or silica gel.

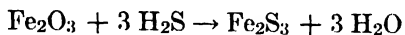
If the gas is warm, it must be cooled before light oil removal, this being best accomplished by direct contact with a water spray. The cold gas passes counter current to the absorbing oil up towers filled with wooden slats. The "benzolized wash oil" passes through a series of heat exchangers to a steam still, and as "debenzolized wash oil" is cooled and returned to the absorption system.

The gas still contains undesirable sulfur compounds, hydrogen sulfide predominating. The amount in the gas at this point is of the order of 200 to 500 grains per 100 cu. ft. Sulfur compounds are undesirable in domestic gas because of the sulfur dioxide produced in cooking and heating stoves but need not be removed from industrial fuel gas. Very little effort is made to remove the relatively small amounts of carbon bisulfide and other organic sulfur compounds, but hydrogen sulfide is gotten out of the gas quite completely. Hydrogen sulfide probably originated from the direct union of hydrogen with the sulfur resulting from the decomposition of pyrite. The sulfur in resinous organic compounds largely remains in the coke, as does a part of the sulfur compounds of humus. The pyritic sulfur is mainly volatilized, but a portion remains in the coke. The sulfate sulfur is largely retained, but undergoes some transformations. More than half of the total sulfur of the coal remains in the coke, and about one-fourth is accounted for in the gas.

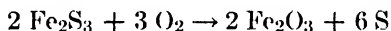
✓ Two methods are used for the removal of hydrogen sulfide from coal gas. The dry or oxide method, which is the older and still more widely used method, is to pass the gas over colloidal hydrated ferric oxide; the newer method washes the gas with various solutions, this being known as "liquid purification."

Hydrated ferric oxide is prepared by mixing iron turnings and borings with wood chips and wetting the mixture with brine or ammonium chloride solution. The iron rusts rapidly, and the ferric oxide forms

hydrates and is rendered colloidal by organic acids from the wood. Wastes from the purification of alumina from bauxite are also quite efficient. The purifier material is charged into steel or concrete boxes through which the gas is passed. Several boxes are used on a single gas line, the bulk of the hydrogen sulfide being caught by the first box. When the material has collected sulfur and sulfides to the limit of its efficiency, a fresh box is made to receive the gas, and the first "foul" box is cut out. Leaving out of consideration the water of hydration of hydrous ferric oxide, which is also liberated, the main reaction is:



Under acid conditions ferrous sulfide forms, which is regarded as undesirable because of the ease with which it forms inert FeS_2 , and alkaline conditions are therefore maintained. When the material in a box ceases to remove any considerable amount of hydrogen sulfide it is revived by oxidation. This is accomplished by passing small amounts of air through the box with the gas, or by cutting out a box and passing air through until it is revived. The process results mainly in the liberation of sulfur and formation of hydrated ferric oxide.



Some ferrous sulfide is inevitably formed, and this is oxidized during revivification to ferrous sulfate, which is easily hydrolyzed to form sulfuric acid. Hence a little lime or soda ash is added to the water sprayed over the oxide while it is being regenerated. If hydrogen cyanide is not previously removed it forms complex cyanides, which remain in the purifier mass. Because of the low price of very pure sulfur, spent oxide is practically a waste product.

Liquid purification is a term that is applied to any process of hydrogen sulfide removal in which the gas is scrubbed by a liquid. Work has been done on liquid purification practically from the beginning of the gas industry, but it has only been a few years since the first successful process was developed. The basis of most liquid purification processes now in use is the removal of hydrogen sulfide by a solution of sodium carbonate. Whatever the mechanism of the reaction may be, the net result is the formation of sodium hydrosulfide along with sodium bicarbonate and sodium cyanide. The gas contains considerable amounts of carbon dioxide in comparison with hydrogen sulfide and relatively minor amounts of hydrogen cyanide.

The detail in which the liquid purification processes differ is the handling of the fouled solution and its reactivation for reuse. The Seaboard Process involves scrubbing the gas in a tower by means of sodium carbonate solution, pumping the fouled solution to another tower, which may be superimposed upon the first tower, and blowing air through the fouled solution to actify it. The air functions purely as an inert gas; the equilibrium reactions are reversed; and hydrogen sulfide, carbon dioxide, and hydrogen cyanide are swept out with air. The contaminated air is best disposed of in furnaces, but may be disseminated by a stack. This process has an efficiency up to 95%, and is often supplemented by iron oxide boxes. There are three processes in which the hydrogen sulfide is broken up by catalytic oxidation with the recovery of sulfur. The "Ferrox" Process, also known as the iron-sulfur process, includes scrubbing the gas by a soda solution containing an iron compound in suspension; passing atomized air through the fouled solution; removal of the sulfur in the form of a thick frothy suspension; and reuse of the activated solution. Some of the catalyst remains in the sulfur. The Nickel Process cannot be used with coal gas unless hydrogen cyanide has been previously removed, since inert double alkali-nickel cyanides are formed. It has some use with oil gas. With the exception of the catalyst the process is the same as the iron-sulfur process. The Thylox Process employs a soluble catalyst, hence the sulfur obtained is quite pure. Absorption is in a tower packed with wooden grids, and activation is carried out in several ways, including the use of atomized air, flotation equipment of the type used in the mining industry, and activation under pressure by means of compressed air passed through the warm fouled liquid. Efficiencies up to 98.5% sulfur recovery are reported.

Such sulfur competes with Texas brimstone, but the tonnages are still quite small. Being very finely divided it has considerable value in agriculture in sprays and dusting powders. In the Seaboard Process some sodium thiocyanate, NaSCN , is formed, and in the others all the hydrogen cyanide ultimately remains in solution as this compound. Some sodium thiosulfate is also formed.

For certain uses even the small amount of carbon bisulfide in the gas is objectionable. By passing the gas over a catalyst at 700°C . to 800°C . hydrogen sulfide is formed and is easily removed.

Since the gas is handled over water, it carries with it water vapor practically up to the equilibrium vapor pressure. Cooling in the distributing system causes condensation, and corrosion is inevitable. Considerable progress has been made in dehydrating gas by washing

it with concentrated solutions of salts, such as calcium chloride, whose vapor pressures are quite low. This process is carried out in connection with oil scrubbing to remove naphthalene after removal of hydrogen sulfide. Oil in the form of a fine mist is added to the dry gas to keep down dust and to lubricate valves in mains.

The foregoing description of the purification of coal gas includes all the common methods for removal of all materials that are undesirable in gas for all uses. The gas from by-product coke ovens, when used as an industrial fuel, ordinarily passes only through coolers, tar extractors, and ammonium sulfate saturators. Light oils are taken out only to meet a limited demand. The removal of hydrogen sulfide is not always necessary.

The purified gas has as its principal combustible components hydrogen and methane, these two gases constituting fully four-fifths of the total volume. All hydrocarbons other than methane and higher paraffins are usually classed as "illuminants" in a commercial gas analysis. In computations they are assumed to be propylene, C_3H_6 , but the term includes ethylene, acetylene, and benzene. A series of analyses of coal gas from retort plants shows the following maximum and minimum values:

COMPONENTS	MINIMUM	MAXIMUM
Methane... ..	26.9	40.5
Illuminants... ..	3.4	4.0
Hydrogen... ..	46.0	52.3
Carbon monoxide... ..	6.0	10.7
Carbon dioxide... ..	0.5	2.5
Oxygen... ..	0.3	0.5
Nitrogen... ..	1.5	9.4
B.t.u....	545	660

A series of typical analyses made on coke-oven gas indicates the differences between gas collected early and that collected late in a run, and between the gas with light oils and gas from which they have been removed.

- No. 1. Total run without removal of light oils.
- No. 2. Total run after removal of light oils.
- No. 3. Gas from early part of run without removal of light oils.
- No. 4. Gas from early part of run after removal of light oils.

No. 5. Gas from latter part of run without removal of light oils.

No. 6. Gas from latter part of run after removal of light oils.

COMPONENTS	1	2	3	4	5	6
Methane.	33.9	34.2	35 0	35.4	27.0	27 3
Illuminants	3 5	2 6	4 2	3.2	2 0	1 0
Hydrogen.	47 3	47 8	46.3	46 8	57 0	57 5
Carbon monoxide	6 8	6 9	6 3	6.4	6 0	6 1
Carbon dioxide.	2 2	2 2	2 6	2 6	2.1	2 1
Oxygen.	0 3	0 3	0 2	0 2	0 3	0 3
Nitrogen.	6.0	6 0	5.3	5 4	5 6	5.7
	100 0	100.0	100 0	100 0	100 0	100.0
B.t.u.	591	562	630	605	528	497

Average yields from one ton of coal are as follows:

Coke.	1400 lb.
Gas.	11,000 to 13,000 cu. ft.
Tar.	9 to 13 gal.
Ammonia	5 to 6 lb., or on an average of 24 lb. ammonium sulfate
Light oils.	3 to 4 gal.

BY-PRODUCTS OF COAL GAS

It now remains to follow each material that has been removed during the foregoing processes and see what products are made from it. The order of removal—tar, ammonia, hydrogen cyanide, naphthalene, light oils, and hydrogen sulfide—will be followed in discussing the products.

Tar Products. Very large quantities of the tar removed from coal gas are burned directly as a fuel, particularly in steel mills. The larger part of all the tar from city gas plants is marketed for distillation. Most of the tar that is processed in any way is used in making roads and roofs and other protective coatings. It is subjected to distillation in order to remove oils and low-melting solids, so that a pitch of the right melting point and consistency may be obtained. Horizontal stills heated by direct fire and stirred by steam continue to find use, although more modern plants are operating with the same type of pipe still that has been so successful in the petroleum industry.

A very thorough study of the composition of coke-oven tar was made some years ago by Weiss and Downs in one of the plants of

The Barrett Company. Ten thousand gallons of distillates from coke-oven tar were used in this investigation. Fractionation of distillable material was carried out in vacuum column stills, which reduced secondary decomposition to a minimum. Following is a summary of what coke-oven tar contains:

Light oils (benzene, toluene, xylene, cumene, coumarone, indene, etc)	2.0%
Middle and heavy oils	23.7%
Naphthalene	10.9%
Substituted naphthalenes	7.3%
Fluorene	1.6%
Unidentified oils	3.9%
	<hr/>
	23.7%
Anthracene oil	12.8%
Phenanthrene	4.0%
Anthracene	1.1%
Carbazol and homologues	2.3%
Unidentified oils	5.4%
	<hr/>
	12.8%
Phenols	2.2%
Tar bases	2.3%
Pitch oils, greases, and resins	12.3%
Pitch (460° F. melting point)	44.7%
	<hr/>
	100.0%

Since pitch of this melting point is rarely made, in an average distillation considerably more than half of the tar is represented by the pitch. For low-melting pitches, much less is removed by distillation. Not more than 6% of all the light oil obtained from the carbonization of coal comes from the tar, the remainder being scrubbed from the gas after all tar has been removed. Since benzene from light oil is used in several times the amount of naphthalene from tar, it is misleading to speak of the "coal-tar dye industry."

The first distillation of tar results in the removal of a mixture of volatile compounds, leaving behind a residue of pitch. The following fractions may be considered as typical.

1. Up to 170° C. Light oil.
2. 170° C. to 235° C. Carbolic oil.
3. 235° C. to 270° C. Creosote oil.
4. 270° C. to 315° C. Anthracene oil (light).
5. 315° C. to 355° C. Anthracene oil (heavy).

The temperatures given here represent averages, separation being governed not by temperature of the vapors, but by tests on the products. *Benzol* and related compounds from the first fraction are combined with the light oil from wash oil scrubbers, and all these materials are refined together. *Naphthalene* is obtained by long settling and crystallization, separated by centrifuging, and purified by recrystallization, distillation, washing with sulfuric acid and caustic soda, and final sublimation. The crude material is often added to wood-preserving oils; the finer grade is used in making dye intermediates. *Phenols* and *tar acids* are removed from those distillates in which they occur in profitable amount by extraction with dilute caustic soda. Soluble phenolates are formed. Practically quantitative separation of the various phenolic substances is secured by using limited amounts of caustic and mixing intermediate extracts. Carbonic acid frees the larger portion of phenol and related compounds from their alkaline solutions, but complete separation requires the use of sulfuric acid, this being due to the solubility of phenolates in phenols. The amount of phenols in coal tar is not large, but is sufficient to meet the demands for oil emulsion disinfectants and sheep and cattle dips. It is not enough to supply pure phenol for such uses as the manufacture of synthetic resin. Synthetic phenol is made in large quantities from benzol from light oils, and represents around four-fifths of all phenol marketed. Since separation of phenol from cresols and the higher tar acids by the initial extraction is practically complete, it is only necessary to purify phenol by distillation and crystallization. *Anthracene*, *phenanthrene*, and *carbazol* are obtained from the higher-boiling fractions from the distillation of tar. These are allowed to stand for several weeks until a solid separates. This is removed by filtration, usually in plate and frame presses. Solvent naphtha mixed with the disintegrated cake removes phenanthrene. Pyridine will dissolve carbazol, leaving behind a crude anthracene. Sublimation serves to purify anthracene. All three substances find use as dye "crudes." Paracumarone resins resulting from coal-tar distillation products find extensive use in varnish making.

The demand for pure compounds from tar distillation is limited, but there is a very widespread use of tar oils as wood preservatives. This material is known commercially as *creosote oil*, and includes the distillate from coal tar boiling above 200° C. and up to a point where pitch of desired melting point is left behind in the still. Specifications for wood preservatives require approximate adherence to distillation, specific gravity, refractive indices of distillates, and tar acid limits,

and even wood distillation tar oils are used for the same purpose. The value of creosote oil and similar materials depends to some extent on phenolic substances, but much more largely on such hydrocarbons as naphthalene, anthracene, and phenanthrene. These substances are very slightly soluble in water, and hence keep out moisture and are not easily removed from the wood. At the same time enough of the hydrocarbon is dissolved in the water to repel all forms of destructive insects. Railroad ties, bridge timbers and piling, and other wooden materials of construction are "creosoted" by immersing them in hot tar oils and applying high pressure. The amount of wood-preserving oils made in the United States is of the order of 130 million gallons per year. Tar oils also find some use as flotation oils.

Aqua ammonia refers to a concentrated water solution of ammonia. It has normally a specific gravity of 0.90 and an ammonia content of 28.5%. This is approximately 26° Bé. Less concentrated solutions known as 20° Bé. and 16° Bé. grades are also available. The method of preparing aqua ammonia consists in warming the weak liquor from tar and from water scrubbers until carbon dioxide and hydrogen sulfide are largely driven out, there being little or no loss of ammonia, and then adding milk of lime and subjecting the liquor to distillation in a column still. The vapors are scrubbed with lime water, caustic soda solution, and oil, and finally passed through activated chars before being absorbed in distilled water. *Anhydrous ammonia* is made by cooling and compressing these vapors without using water at all. *Ammonium sulfate* is the product of the ammonia recovery process used in many coke-oven plants. The indirect process consists of scrubbing out all the ammonia from the gas with water, and purifying this ammoniacal liquor partially by heating it. That portion to be made into ammonium sulfate is fed into the column of a still where the heat and rising vapors drive out ammonia from ammonium hydroxide and ammonium carbonate solutions. The salts of strong acids such as sulfate and chloride are broken up in the lower part of the still by adding a suspension of calcium hydroxide and introducing steam. The vapors from the still pass to the saturator, which is a lead-lined steel vessel containing a saturated solution of ammonium sulfate and sufficient sulfuric acid to maintain its concentration approximately that of a normal solution. The vapors are intimately mixed with the liquid by escaping from beneath the serrated edges of the inlet pipe. The heat of reaction causes sufficient evaporation to keep the volume in the saturator constant. Waste vapors pass through a condenser, and the fixed gases pass to the nearest coke oven

or boiler firebox to be burned and thus obviate a nuisance. The condensate is very offensive in odor, and is either run through spent oxide and mixed with still wastes or run directly into soil. Still wastes are particularly objectionable in streams, since they contain phenolic bodies which will kill fish. Phenols may be removed from such liquors by treating with hot inert gases and scrubbing the evolved gases with caustic soda. Activated carbon may also be used to remove phenol from ammoniacal liquor, the phenols being extracted from the carbon at intervals by benzol or steam.

Ammonium sulfate crystallizes in the saturator, and the crystals are removed continuously and automatically from the saturator by means of steam ejectors or compressed air, charged into centrifugals, and freed from adhering solution. The product is practically pure and dry, and is sent to storage.

The direct process involves cooling the gas with tar and ammoniacal liquor, collecting all ammoniacal liquor from mains, condensers, and tar extractors, distilling ammonia from this liquor back into the gas, and scrubbing ammonia from the preheated gas in saturators by means of dilute sulfuric acid. The only difference in this part of the operation between the direct and indirect processes is that the removal of ammonia from a large mass of gas requires a larger saturator. Ammonium sulfate finds its chief use as a fertilizer material.

If hydrogen cyanide is removed in a separate process from that used to take hydrogen sulfide from coal gas, the products that find their way to the chemical market are *calcium ferrocyanide* and sometimes *ferrous ammonium ferrocyanide*. Liquid purification methods result in the formation of *sodium thiocyanate*.

Naphthalene scrubbed from gas is recovered by distillation of the scrubbing oil and crystallization. It is common practice, however, to mix the oil saturated with naphthalene with creosote oil to increase its value as a wood preservative.

The production of *light oils* involves scrubbing them from the gas by a high-boiling oil, preheating this solution of light oils first by vapors and second by hot still residues, and distilling with steam. The distillate, which amounts to around four gallons of light oils per ton of coal carbonized, is approximately one-half *benzol*. A distillate made up of 70% of the total light oils would function satisfactorily as a motor fuel. The degree of fractionation depends on the purity of the material desired. By use of column stills it is possible to obtain very pure benzol, toluol, and xylols, the higher-boiling residues being

used as solvents without further separation. The yield of *toluol* is about one-seventh the weight of the crude light oil; the *xylois* run something over one-half the weight of the toluol.

LOW-TEMPERATURE CARBONIZATION

Since the main object of high-temperature carbonization is the production of a marketable gas and coke, until recently very little attention has been paid to processes that avoided secondary decompositions in carbonization. Because of the waste of combustibles and the large amount of smoke and consequent soot which characterize the combustion of bituminous coal in stoves and small furnaces, anthracite has been very extensively used as a "smokeless fuel." Anthracite coal is produced in only a very limited area in the United States, most of it coming from one district in Pennsylvania. Hence cost of transportation makes its general use impossible in comparison with that of soft coal. There is thus a very real and large demand for a comparatively smokeless domestic fuel. The intermediate sizes of coke are partially satisfying this demand, but the gasification of coal depends most largely on the market for gas and metallurgical coke. There is also a field for low-temperature coke as a material to be mixed with high-volatile coal as a feed for coke ovens.

Among the problems and difficulties of low-temperature carbonization the following may be mentioned. Coal conducts heat very inefficiently so that complete carbonization takes place in the portion being heated before any change has occurred in the portion most distant from the source of heat. At a certain stage, coal becomes sticky and plastic. Thin layers mean excessive cost of equipment. Mechanical stirring produces a very weak coke. If the product is briquetted, the binders are smoke-producing and the briquettes must be carbonized. At the stage at which the semicoke should be pushed it has expanded, which makes removal most difficult. The coke is very hard to quench, and also burns too rapidly for the average house furnace, being better adapted for open fireplaces. The hydrocarbons from the tar are largely non-aromatic. The creosote oil from the tar does not meet prevailing wood-preservative specifications, and only long-time tests can prove its efficiency in this field. The higher phenols obtained in good yields from the tar develop a pink color in emulsions, and it has so far been impossible to overcome the prejudice of sheep and cattle raisers against using these emulsions as "dips." These same phenolic substances do not form quick-curing resins and plastics in combination with formaldehyde.

In spite of all these difficulties, which some practical gas men consider to have been largely overcome, low-temperature carbonization might have begun to be of industrial importance had it not been for the vast resources of natural gas that have become available in recent years and for enormous overproduction of petroleum and consequent low fuel prices. Since these conditions do not exist in Europe there

is still great interest there in low-temperature carbonization. Not only are new processes being developed, but there is very considerable production of low-temperature coke by existing processes.

Some of the devices that have been tried in the low-temperature carbonization field are these. Coal is heated in thin layers in tubes cast in a solid block of iron. Carbonization is carried out in a horizontal retort equipped with paddles to stir the heated coal. A double retort made up of two concentric cylinders has been used, the coal being preheated in the inner cylinder and carbonized in the outer annular space of the retort, which is heated on the outside. A part of the semicoke made in a large vertical retort is fed into a producer below the retort, and carbonization of the contents of the retort takes place because of the effect of the hot producer gas. In two stage processes the coal is dried, a part of the oxygen content is removed, and exothermic reactions are started in the first stage.

BLUE GAS AND PRODUCER GAS

There are three kinds of industrial gas made primarily from coke by the action of air and steam, which are related to each other by their main chemical reactions. Blue gas, sometimes called water gas, results from the action of steam on heated fuel. Carburetted water gas is blue gas to which freshly prepared oil gas is added. Producer gas is made by the continuous passage of a mixture of air and steam through a bed of fuel. Coke is used to a very large extent as a fuel, hence the making of these gases depends on previous carbonization. If anthracite coal is used, there is a slight amount of carbonization, since this type of coal evolves small amounts of volatile material on heating. Where soft coal is used, there is the preliminary carbonization of the fuel and the formation of a sort of coke before the gasification reactions begin.

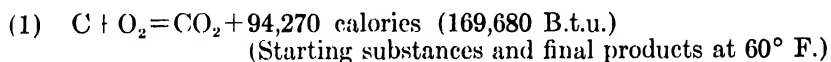
Blue Gas. When steam is passed over highly heated carbon, the products of the reaction are primarily carbon monoxide and hydrogen. These two gases burn with a non-luminous flame, and each has a heating value of about 330 B.t.u. per cubic foot. For these reasons blue gas will not meet the specifications of cities. A great deal of blue gas is used by industries that require a gas of higher heating value than producer gas. Some blue gas is used to mix with natural gas and coal gas.

The principal piece of equipment used in making blue gas is the generator. This is essentially a steel cylinder lined with firebrick and equipped with grates, clean-out doors, a charging opening at the top, steam and air pipes, and an outlet for the gases. This outlet connects

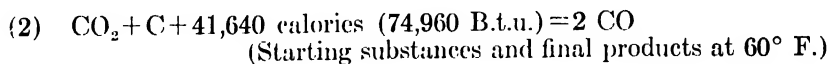
with a stack valve, which is equipped with a pilot flame. When the stack valve is open, the gas from the generator escapes either to the air or waste heat boilers. When it is closed, the gas passes to a wash box, sometimes called a "seal-separator," which functions in the same way as the hydraulic main of a coal gas retort, the inlet pipe opening being just below the level of the water. The gas is then conveyed either to scrubbers or directly to burners.

The fuel used in the generator is most commonly coke. Anthracite coal is excellent fuel but is ordinarily too expensive. The coke is usually not over 2.5-in. material with "breeze" up to 0.5 in. screened out. In recent years, bituminous coal has been extensively used, particularly in the "back run" process, described later.

The reactions which take place are divided into two groups. When air is blown through the fuel bed to raise its temperature, the first reaction is the result of contact between oxygen of the air and the carbon of the fuel.



(The value given here is lower than that ordinarily given in textbooks for the heat of combustion of crystalline carbon, but probably represents very closely the heat available from the combustion of carbon in commercial fuel.) Any hydrogen present in the fuel burns to steam, and this in turn reacts with the carbon of the fuel. Carbon dioxide in contact with carbon at the high temperature of the fuel bed would be reduced quantitatively to carbon monoxide if the time of contact were sufficient.

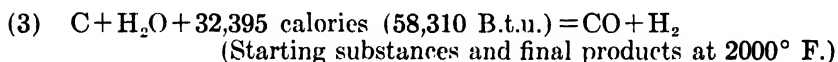


The object of the "blow," however, is to heat the fuel to a sufficiently high temperature to make as much carbon monoxide and hydrogen as possible in the next step of the process. Hence air is driven through the fuel bed at such a rate that the main product of the reaction is carbon dioxide. Pressures of the order of 40 in. of water are commonly used. The nitrogen of the air dilutes the other gases and thus reduces their partial pressures still more, so that equilibrium is never attained. The hot gases preheat the coke in the upper part of the charge. The gases escape through the stack valve, and formerly were merely wasted, the carbon monoxide being ignited by the pilot flame. Waste

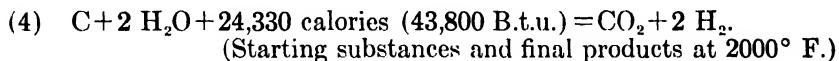
heat boilers and accumulators are being extensively used to recover a part of the heat.

In order to avoid excessive temperature at the sides of the generator and the accumulation of a dense and partially burned central section, some generators have been provided with refractory central piers.

When the fuel bed is sufficiently hot, the air blast is cut off and steam is admitted to the generator under low pressure, the steam often being superheated. The steam may follow the same path as the air blast, but most sets are equipped so that a part of the runs are "down runs," the steam going from the top of the fuel down through the grate bars and into a gas outlet at the bottom of the generator. All down runs begin and end as "up runs" and are for the purpose of preventing the gradual creeping up of the oxidation zone and excessive temperatures at the top of the generator. After a few seconds, during which the blast gases are swept out, the stack valve is closed and the blue gas is passed through the wash box to scrubbers, or directly to burners. The main reaction by which blue gas is made by the action of steam on carbon is



(The values often given in reference books refer to liquid water, whereas the material actually used is steam. Hence the temperature of 2000° F. for the starting substances and final products has been given here.) Of minor importance is the production of carbon dioxide by the reaction



The carbon dioxide formed is rapidly reduced once more to carbon monoxide by the hot carbon. Inside of three or four minutes the rate of these reactions has greatly decreased. The amount of carbon dioxide formed has become greater than that of carbon monoxide. Hence it is necessary to raise the fuel bed to a temperature at which rate of reaction is rapid and carbon monoxide is formed rather than dioxide. The steam is cut off, and air is again turned on. This succession of run and blow is followed continuously, being interrupted in ordinary practice only at intervals when fresh fuel is charged. After several hours, the older and still most widely used type of generator

must be shut down to remove the ash and clinker from the generator. Some modern generators are equipped for automatic charging at each complete cycle, and also with self-clinkering grates by means of which the clinker is cut from the fire. The clinker is crushed through the grates and discharged around the periphery of the generator. There is the record of one installation being run 1900 hours without interruption. Automatic feed and discharge means from 12% to 18% increase in output, a more uniform gas, less excess heat, and less carbon in the ash.

Carburetted Water Gas. The term water gas is used to include both blue gas and carburetted blue gas, which is very generally called carburetted water gas. The production of carburetted water gas differs from that of blue gas mainly in the handling of the blow gases after they have left the generator. Formation of a certain amount of carbon monoxide during the air blast is inevitable, but in making blue gas just as little carbon monoxide as possible is formed. In making carburetted water gas, carbon monoxide in the blow gases is highly desirable, since it is utilized to heat the remainder of the gas-making equipment.

A carburetted water gas set differs from a blue gas set in the introduction of two additional pieces of equipment, the carburetter and the superheater. Both of these are ordinarily vertical steel cylinders lined with firebrick and packed with checker set firebrick. The superheater is considerably taller than the generator and the carburetter. The carburetter is connected near the top with the generator outlet pipes, and has equipment for spraying oil downward on the checker brick packing. The gas outlet from the bottom of the carburetter passes to the base of the superheater, and the discharge pipe is connected with the stack valve and the remainder of the system, which includes a wash box and condenser. A single shell carburetted water gas set is used by a number of plants. The generator occupies the bottom portion of the shell and is cylindrical, while the carburetter and superheater are side by side and each are of D-shaped or semi-cylindrical cross section.

The blast gases from the generator enter the top of the carburetter, and enough air is admitted to the carburetter at the same time to burn the carbon monoxide present. In some plants, additional air is added in the superheater. The effect of this combustion and the sensible heat of the blast gases is to raise the temperature of the checker brick to the point required for making oil gas. The hot gases from the carburetter are sent to the base of the superheater, and give

up a large part of their heat to the packing of this part of the set. The combustion of carbon monoxide also continues in the superheater. The waste gases either escape through the stack or go to waste heat boilers.

When the blast is cut off, steam is admitted to the generator, and gas oil is sprayed down into the carburetter. This oil has been described in connection with petroleum refining as a relatively high-boiling mixture of hydrocarbons resulting either from the direct fractionation of crude oil, or more commonly at the present time from the distillation of the residues of various high-pressure cracking processes. Even some "topped crudes" and heavy oils are used. When heavier oils are used for enrichment the checker brick are removed from the carburetter and only a part of the oil is introduced into it. The remainder of the oil is sprayed directly on top of the hot coke in the generator during both up and down runs. Considerable coke is formed on down runs, but is burned out readily during the blow and is a cheap fuel. The reactions involved in the pyrolysis of high-boiling hydrocarbons are quite complicated and cannot be simply represented by a few equations. The net result is the formation of hydrogen, methane, ethane, lower olefins such as ethylene and propylene, small amounts of aromatic hydrocarbons, and tar.

The blue gas sweeps the oil out of the carburetter as rapidly as it forms. Under the influence of heat and the large and porous surface of the firebrick in the superheater, reactions take place between the components of the water gas and oil gas, most of which are probably hydrogenations of unsaturated hydrocarbons. The composition of the resultant "carburetted water gas" is not the same as that of a mixture of water gas and oil gas made in the cold or even calculated on the basis of the composition of the two separately. The heating value is higher than that of the mixture, and the amount of unsaturated hydrocarbons is less.

The control of valves for steam and oil was once entirely by hand, which naturally introduced variations of 10 to 15 seconds in intervals. Now in large sets all valves are moved by compressed air, by water under pressure, or by motors, and are often automatically controlled.

Carburetted water gas is not successfully handled in waste heat boilers because of deposition of tarry material in the tubes, but the blast gases are very commonly sent through such a heat-recovery system. The water gas passes through a wash box equipped with baffle plates for removal of tar, and thence through a surface condenser. The gas is then sent to a small "relief" holder, which serves

to equalize the pressure. In coal gas production the operation is continuous, and uniform pressures are continually maintained. The blue gas and carburetted blue gas processes are intermittent, but purification processes should be continuous. Hence it is necessary to provide a small holder to collect the gas and pass it on uniformly. The relief holder may precede the condensers. Exhausters of much the same type as those used in the coal gas industry are employed in handling carburetted water gas, and are usually located just ahead of the tar extractors. The purification system resembles somewhat that of a coal gas plant except that no provision need to be made for removal of ammonia. Extractors of the P. and A. type and Cottrell electrostatic precipitators are used for removal of tar. Light oil yields are higher than those from coal gas, water gas carrying about 0.5 gallon per thousand cubic feet, whereas coal gas rarely has over 0.3 gallon. If the checker brick temperatures are too high, excessive amounts of naphthalene are formed. It is not common practice to remove the light oils from carburetted water gas unless the price of these materials is high, since by such removal there is some lowering of the heating value of the gas. During the war period, toluene was very much in demand, and some plants scrubbed light oils very thoroughly from the gas, fractionated out the toluene, and put the benzene back into the gas. Hydrogen sulfide is removed most commonly by hydrated ferric oxide, the only difference between the practice with water gas and coal gas being that the temperature at which hydrogen sulfide is taken out of the gas is somewhat higher in order to avoid condensation of benzene. Liquid purification is also entering this field. Instead of the use of gas oil some blue gas is enriched by the addition of propane-butane mixtures from the gasoline recovery process in which natural gas is freed of all condensable hydrocarbons followed by removal of the lighter ones from the gasoline. Still gases from petroleum refineries may take the place of gas oil for enrichment.

A carburetted water gas set with a generator 11 ft. in inside diameter, which may be taken as an example, will produce from 4,000,000 to 5,000,000 cu. ft. of gas per day. It is estimated that one ton of coke will produce about 55,000 cu. ft. of blue gas of around 300 B.t.u. heating value, and to this is added enough oil gas, which has a very high heating value, to bring the gas which leaves the superheater to around 525 B.t.u.

Typical operating data on a carburetted water gas plant indicate that for each 1000 cu. ft. of 550 B.t.u. gas from 26 to 33 lbs. of fuel are required in the generator; from 30 to 45 lbs. of steam are used,

of which about one-half is decomposed; the consumption of oil is from 3 to 3.5 gallons; and the air used with anthracite coal in the generator is 1400 to 1800 cu. ft., and with bituminous coal from 1000 to 1400 cu. ft. A typical blue gas analysis shows the following values:

Methane	0.7
Hydrogen	47.3
Carbon monoxide	43.5
Carbon dioxide	3.5
Oxygen	0.6
Nitrogen	4.4
	<hr/>
	100.0
B.t.u.	302

A series of carburetted water gas analyses are given below. In these, ethane is included with methane, and benzene is regarded as an illuminant. No. 1 is quite a bit higher than the average and shows what can be done with heavy enrichment, while No. 3 is below the usual city specifications, and was made by carburetting with butane.

	1.	2.		3.
Methane	17.0	13.7	Methane	2.8
Illuminants	13.6	9.3	Butane	8.8
Hydrogen	33.2	32.5	Illuminants	0.6
Carbon monoxide	29.8	30.9	Hydrogen	29.7
Carbon dioxide	3.0	3.4	Carbon monoxide	26.7
Oxygen	0.5	1.3	Carbon dioxide	4.8
Nitrogen	2.9	8.9	Oxygen	1.0
	<hr/>	<hr/>	Nitrogen	25.6
	100.0	100.0		<hr/>
				100.0
B.t.u.	649	552	B.t.u.	508

Water Gas By-Products. The tar from water gas is much lower in specific gravity than coal-gas tar, contains less free carbon, and is practically free from tar acids. It also has less naphthalene and contains some unchanged paraffin hydrocarbons. It is apt to form emulsions with water which are hard to break up. A comparison of the average composition of the crude light oils from water gas and coal gas is as follows:

	COAL GAS	WATER GAS
Benzene	60%	25-35%
Toluene	10-20%	20-30%
Solvent naphtha	10%	15%
Higher paraffins and unsaturated compounds	10-20%	20-40%

The "Back-Run" Process. The fuel used in making water gas, both in the blue gas and carburetted water gas processes, is commonly coke. A process that uses soft coal as well as coke has been developed and is in successful use in several plants. If soft coal were used and the blast and blow followed the same path as described above, the carburetter and superheater would soon clog with carbon deposits. The "back-run" feature is said to get rid of this trouble. Every other run, steam is admitted at the top of the superheater and passes back through the set in just the opposite direction to the ordinary way. In this process all the tar and carbon are converted to blue gas by the steam. The gas made in the back run is led to the wash box. Oil is sprayed into the carburetter only in "up runs," in which the usual routine is followed. A typical cycle is:

Blow	2 minutes
Up run	2 minutes
Blow	2 minutes
Back run	2 minutes
Up run	1 minute

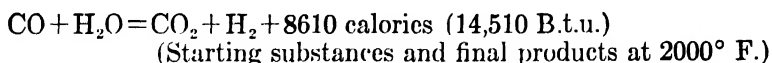
The back-run process is possible where a heating value of not more than 530 B.t.u. is required, and where there are no candlepower standards. The saving of fuel amounts to around two pounds per thousand cubic feet of gas made. Although originally designed for use with soft coal, the "back-run" process finds use in a number of plants employing coke. A few plants follow the ordinary blow by a reversed air blast, the process resembling the back-run process except that air is substituted for steam.

Reformed Gas. Refinery gas, natural gas, and the very volatile liquids removed from natural gas may be used to enrich blue gas. It is ordinarily necessary to subject these gases to a "reforming" operation. This is commonly accomplished in the case of fixed gases by blasting the fuel bed with air and then passing the enriching gas and steam through the fuel bed. Reforming thus includes cracking of hydrocarbons, and both blue gas and producer gas reactions. Reforming is also carried out in oil gas generators of various types. Propane-butane mixtures separated from natural gas are commonly mixed cold with blue gas in order to produce enrichment.

Producer Gas. The making of water gas is an intermittent operation, requiring complicated valves to provide for alternate blasting with air and blowing with steam. Continuous passage of air and steam together through a heated bed of fuel results in a gas of low

heating value, but the operation is relatively very simple. The gas is used generally without purification or storage as rapidly as it is made. Air alone will give a gas of somewhat lower heating value, and steam has the added advantage of avoiding excessive temperatures near grate bars. The gas made by passing air and steam continuously through heated fuel is known as producer gas. Practically all furnaces are producers, but the gas made is burned above the fuel bed, whereas producer gas is removed and burned at localized points throughout the plant.

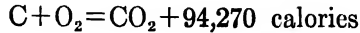
When the oxygen of the air comes in contact with the ignited coke, Reaction (1) takes place. The presence of steam at this point takes up part of the heat liberated, hence serves to keep down the temperature and prevents fusion of the ash. All the oxygen is removed before the air has passed more than a fraction of an inch through the hot fuel. Steam reduces the temperature of the fuel bed in two ways. It serves to dilute the air, and being at a much lower temperature it takes up heat. If any steam is decomposed, the hydrogen would immediately combine with the unused oxygen of the air to form steam again. As soon as all the oxygen is removed, the steam reacts with the carbon of the fuel according to Reactions (3) and (4). At the high temperatures above the combustion zone, carbon dioxide reacts with hot carbon to give carbon monoxide as represented by Reaction (2). Carbon monoxide is quite stable, and the time of contact between carbon and carbon dioxide is much greater than in the blast of a blue gas set. Hence, equilibrium, which at high temperatures is practically completely in the direction of carbon monoxide formation, is approximately attained. The hot gases serve to preheat the fuel that is above the region where radiation is the primary effect. Unchanged steam causes a reaction to take place above the fuel bed that serves to reduce the amount of carbon monoxide and increase hydrogen:



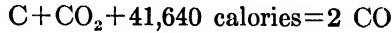
Since the two gases have the same heating value, there is no loss in the gross heat value of the final producer gas.

If air alone were used in a producer and the gas so made were allowed to cool to the same temperature as the entering air, the loss in heating value in comparison with burning carbon directly would be about 30%. This is evident by the following considerations. Two

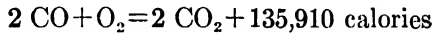
mols of carbon are involved. The first mol burns with oxygen to give carbon dioxide:



The second mol reduces the carbon dioxide to give two mols of carbon monoxide:



If these two mols of carbon burned directly, they would have produced 188,540 calories. The two mols of carbon monoxide burn with oxygen to give 135,910 calories:



$$135,910/188,540 \times 100 = 71\%$$

The use of steam, the substitution of bituminous coal, and the employment of waste heat boilers reduce this loss so that it may not be over 15% instead of 29%. Steam alone, as in the water-gas process, produces a gas of about 300 B.t.u., whereas true producer gas made by air alone is never over 110 B.t.u. because of the dilution by nitrogen.

When anthracite coal is used, the conditions are much the same, since the amount of volatile matter is low and the heating value of the gas due to addition of coal gas is not much above that of a coke-fired producer. Bituminous coal undergoes carbonization, first by the heat of the gases, and then by the heat of radiation of the fuel bed. Thus the producer gas is enriched by coal gas. Non-caking coal must be used in an ordinary producer, owing to clogging because of fused masses that characterize caking coals.

The chief limitation on a producer fuel is the fusion temperature of its ash. If this is low, the producer must be run at such a low temperature that it is not efficient. With an ash of a high fusion point the producer can be run at a temperature within 50° C. to 100° C. of this value. Some European producers use air alone and deliberately fuse the ash and withdraw it as a molten slag after the fashion of a blast furnace, but this practice is practically unknown in the United States.

Assuming the use of bituminous coal, a producer may be regarded as being divided into four zones. At the bottom is a layer of ashes. The air and steam may pass through the *ash zone* if the grate bars are used, or these gases may be fed at a point near the level up to which ashes are allowed to accumulate. Above the ash zone is the

combustion zone. This is relatively thin and is at a very high temperature. It is essential that the rate of feed of air and steam be so adjusted that the temperature does not reach the point of ash fusion at any place. Heat from this zone radiates into the fuel above it, and the hot gases carry heat into the layers above the combustion zone. The *reduction zone* begins at the point where all the oxygen has combined with carbon. The lower part of this zone is at a high temperature, and the reactions take place very rapidly. Since all reactions are exothermic, the temperature is quickly reduced to a value where the speed of reaction is so slow that no further reduction takes place. The last zone is the *preheating and distillation zone.* There is still sufficient sensible heat in the gases to raise the coal to a point where it undergoes low-temperature carbonization, and the products of pyrolysis pass off with the producer gas.

The general principle of all producers is thus to employ a deep bed of fuel, replenished from the top at frequent intervals, to pass steam and air through the fuel bed, and to remove ashes from the bottom of the producer. The fuel is coarsely ground and is for the most part between $\frac{1}{8}$ -in. and 1-in. sizes. Producers may be classified in a variety of ways. Most successful producers are "up-draft," the air and steam passing in at the base of the producer and the finished gas being drawn off at the top. When bituminous coal is the fuel, the gas contains soot and tar. A "down-draft" producer admits the air and steam at the top, so that they pass down in the same direction as the fuel. In spite of the fact that they give a clean gas, mechanical difficulties make their use quite limited. Producers are either of the suction or pressure type. Suction producers use air that has been saturated by contact with warm water, and suction is obtained by a stack, by an exhauster, or by direct connection to a gas engine. Pressure is secured by steam injectors or by a steam-driven turbo blower. The blast is often preheated by the exit gases by means of heat exchangers. Hand-fired and hand-poked producers are used only in small plants; larger installations accomplish both these operations by mechanical means. The fuel bed may be stirred by water-cooled poker bars or rakes, or merely leveled by bars. The ashes may be removed continuously so that operation is never interrupted and each zone remains in practically the same position, or large storage space may be provided and ashes taken out after several hours' run. This procedure necessitates interruption of regular gas making until cleaning is finished. Most producers are of circular cross section and approximately uniform diameter, except in some cases there is con-

striction towards the bottom. The shell may revolve while the top is stationary, or the shell may be stationary and only stirring and leveling devices movable. Suction producers use grates, which are moved to facilitate passing of ashes through them. Most pressure producers operate without grates, the ashes accumulating in a pan from which they are periodically or continuously removed after being wet with

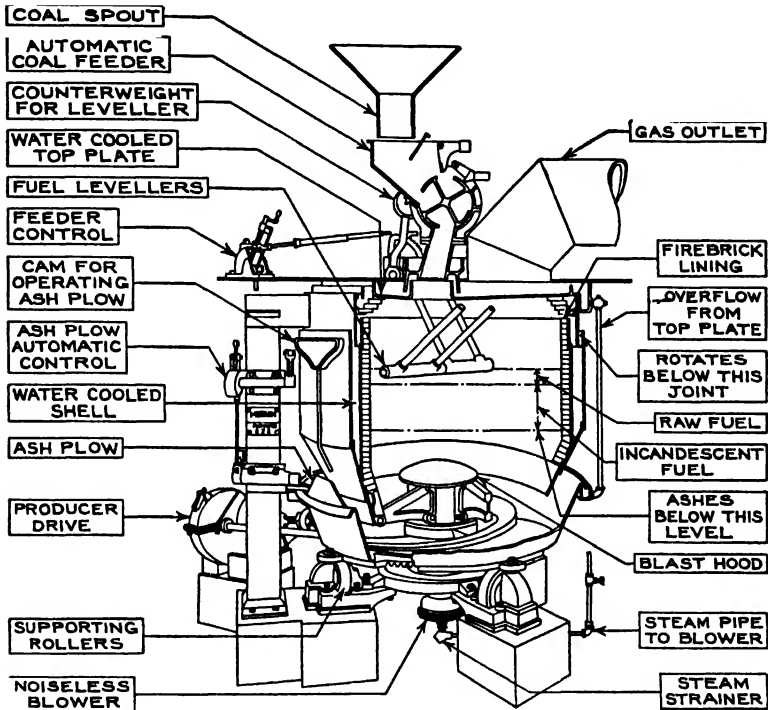


FIG. 129.—Morgan Producer Gas Machine. Courtesy Morgan Construction Company, Worcester, Mass.

water. The water around the periphery of the ash pan also serves to seal the bottom of the producer.

When producer gas is to be burned directly in furnaces, it need not be cleaned. If it is to be used in gas engines, transported any distance, or stored, it is cooled and cleaned. Waste heat boilers serve as economical first units in the cooling system. Anthracite- and coke-fired producers make a gas that is very simply cleaned by dust catchers, washer-scrubbers, and filters packed with coke or wood shavings. Bituminous coal forms a high-melting pitch that hardens into tiny

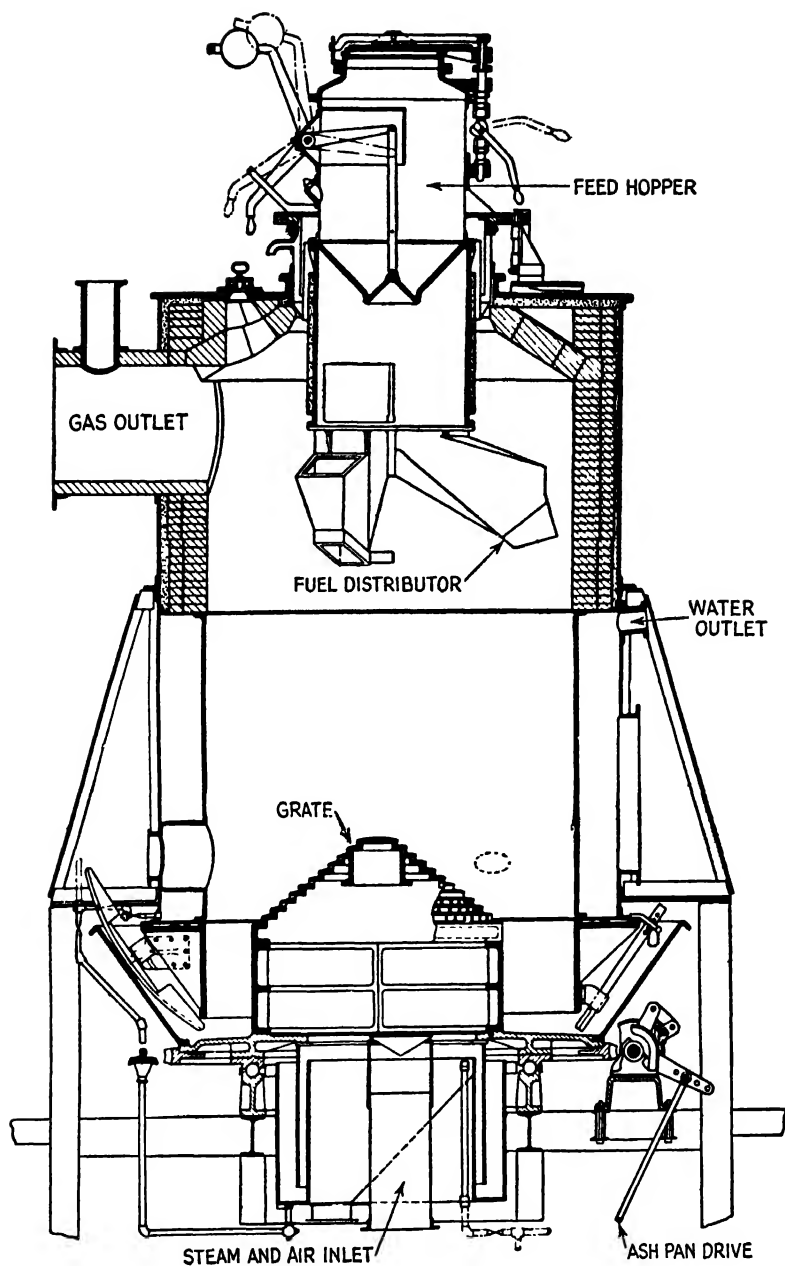


FIG. 130.—Koppers Producer. Courtesy The Koppers Construction Company, Pittsburgh, Pa.

pellets, which are hard to remove from gas. Ordinary P. and A. tar extractors are built for liquid tar, hence filters and electrical precipitators must be used. There is a distinct advantage in cooling producer gas, since a large part of the moisture is removed, which is an important consideration in producers used in connection with coke ovens.

The by-products of producer gas are of negligible value. The Mond by-product producer is used to a considerable extent abroad, and is designed and operated to secure a high yield of ammonia. This producer employs superheated steam along with the air in higher proportion than in ordinary producers, the fuel bed is deeper, and considerable space is provided in the upper part to make possible low-temperature carbonization. On account of the large amount of steam, the temperature in the producer is low, and steam is condensed from the gas before it is used. An acid tower removes ammonia from the gas after it has been partially cooled in heat exchangers, and the hot water from the cooling tower through which the gas is passed after acid removal is used to saturate the air used in the producer. Nearly two-thirds of the nitrogen of the coal is recovered as ammonium sulfate, and considerable tar is obtained.

Some typical analyses of producer gas are given below:

	1	2	3
Methane.....	0 4	2 5	6 3
Illuminants.	none	0 4	0 2
Hydrogen.....	13 2	12 0	10 4
Carbon monoxide ...	25 3	27 0	17 6
Carbon dioxide.....	5 4	2 5	7 3
Oxygen.....	0 6	none	0 7
Nitrogen.....	55 1	53 6	57 5
B.t.u.	137	157	161

The heating value of producer gas from coke and anthracite coal is usually between 125 and 135 B.t.u.; bituminous coal gives averages of about 165 B.t.u. with 180 B.t.u. under the best conditions. Values as high as 215 B.t.u. are known, but it is rare that a gas of this value is obtained. It is obvious that the use of oxygen instead of air will cut down the amount of diluting nitrogen so that a gas of considerably higher heating value than ordinary blue gas can be obtained by use of bituminous coal as fuel. There are excellent prospects of cheap and

abundant oxygen supplies in the future, but at present there is practically no use of oxygen in gas producers.

The production of a low-value gas from pig-iron blast furnaces, used entirely in stoves to preheat the blast and as a fuel in gas engines and under boilers in the plant, is described in the chapter on Metallurgy.

COMPLETE GASIFICATION OF COAL

Strictly speaking, complete gasification means starting with any solid or liquid fuel and converting all of it except a non-combustible residue into fuel gas. This is accomplished in a producer, but the heating value of the gas is low. Bituminous coal is carbonized to form coal gas and coke, and the resulting coke is run in a carburetted blue gas set, both processes making a gas sufficiently high in heating value to meet industrial and public service requirements. This two-stage process, however, requires special types of coal and involves considerable heat losses.

What is commonly referred to as "complete gasification" is the carbonization of bituminous coal with a good yield of high-grade gas, recovery of all by-products, and making gas from the coke, all in one piece of equipment and as a single-stage operation. Theoretically, 40% greater quantities of heat can be realized in a single-stage process in comparison with a two-stage process. This ideal has never been fully reached, and in the United States practically no gas is made in complete gasification units. However, several types of equipment have been developed abroad, which have some promise of success.

The Mond producer is a complete gasification unit, but as generally operated it yields a low-grade gas. In the Wollaston producer the coal is coked in a series of trays above the producer. The Tully complete gasification process uses the gases from the blast to heat the walls of the retort in which distillation takes place, and the water gas formed serves to sweep out intermittently the products of distillation. The Di-Gas process burns the blast gases of a water-gas generator around a carbonization retort, and the hot blue gas is passed through the coal. In the Tri-Gas process air is passed through fuel in a generator of special shape, and the waste gases go through a heat-recovery system. After this, steam passes through the fuel, and the blue gas is sent through the coal in the carbonizing section. In order to secure further heating, a limited amount of air is added to the blue gas as it enters this section, and a portion of the blue gas is burned.

Most complete gasification processes make a gas of 350 to 380 B.t.u. for which there is a very limited demand in this country. Whether

or not complete gasification makes any progress in the United States is a matter of economics, depending on the petroleum situation and the demand for coke as a household fuel.

Statistics of the Gas Industries. Statistics on producer gas are likely to be quite incomplete, since practically all producer gas is made by its consumers. Probably not more than one-fourth of all coke-oven gas is sold to the gas industry for distribution to customers. The relative amounts of different fuel gases produced and purchased by the gas industry for distribution to consumers in 1930 were as follows:

Water gas	37.3%
Coke-oven gas	29.5%
Natural gas	22.5%
Coal gas	7.4%
Oil gas	3.3%
	<hr/>
	100.0%

The uses of fuel gases are distributed as follows:

Domestic	64.1%
Industrial and commercial	29.9%
Househeating	5.5%
Miscellaneous	0.5%
	<hr/>
	100.0%

The magnitude of the gas industry may be realized from these data. In 1930 the industry used 13,613,000 tons of solid fuel and 1,826,400 barrels of oil in the manufacture of gas. A population of nearly 60,000,000 is served by the gas industry, representing more than 12,000,000 customers. The number of miles of mains necessary to distribute this gas is more than 112,000. The total amount of gas distributed to customers amounted to 573.4 billion cubic feet.

In 1930, by-product coke production amounted to 45.5 million tons and beehive coke was 2.75 million tons. The gas made in coke ovens during that year was 720 billion cubic feet. Light oils amounted to 170 million gallons, and tar to 580 million gallons. The total ammonia recovered during 1930 in terms of ammonium sulfate was 725,000 tons. These figures are on the whole considerably lower than those for 1929, coke from ovens being only about 85% and from beehive ovens less than 43% of 1929 production.

Discussion of the storage and distribution of manufactured gas is beyond the scope of this text. The handling, measurement, and storage of gases in general are all briefly described in Chapter VII.

CHAPTER XXV

SYNTHETIC AROMATIC DERIVATIVES

The development of coal carbonization has made available several most valuable compounds which are by-products in the purification of coal gas. From these substances a very large number of derivatives have been made by synthetic methods, and these derivatives occupy a most important position in chemical industry. There are eight compounds of special importance that are by-products of coal distillation:

Benzene, C_6H_6 .

Toluene, $C_6H_5CH_3$.

Xylene, $C_6H_4(CH_3)_2$.

Naphthalene, $C_{10}H_8$.

Anthracene, $C_{14}H_{10}$.

Phenol, C_6H_5OH .

Cresol, $C_6H_4(CH_3)(OH)$.

Carbazol, $C_{12}H_{11}N$.

All these compounds may be obtained in the distillation of coal tar, but the amounts of the benzene, toluene, and xylene are small in comparison with those obtained from coal gas. Although considerable quantities of phenol are gotten from the distillation of coal tar, it constitutes only a small fraction of the distillable portions of the tar, and a great deal more is made by synthetic methods from benzene. Regardless of the purity of these compounds, they are known in the chemical industry as "crudes."

The pharmaceutical, explosive, and dye industries are the three which use the bulk of these compounds as starting substances in the synthesis of more complex derivatives. Many synthetic drugs are made from substances other than those of the aromatic series. Inorganic nitrates and organic esters of nitric acid, such as glycol, glycerol, and cellulose esters, are important components of explosives. Hence these two industries are only partially dependent upon by-products of coal distillation. Although a few dyes are inorganic in their origin, and some dyes are made in considerable amounts from plants of various sorts, by far the largest number of all dyestuffs are made from aromatic compounds from the coal-distillation industry. Except for a period of special demand during the World War when vast quantities of toluene were needed to make the important explosive trinitro-

toluene (T.N.T.), coal distillation has produced a great deal more of these substances than could be absorbed by chemical industry. The actual cost of the starting substances of all of these industries is relatively low, most of the value of the final product having been added by manufacture. Many of these derivatives are quite complex, and all require expert supervision and the highest grade of analytical control in their production; in many cases they are made in relatively small units.

The reactions employed in making synthetic aromatic derivatives include practically all the types known to organic chemistry. Of these the most important are nitration, reduction, sulfonation, amidation, diazotization, coupling, and alkali fusion of sulfonates. In recent years the development of high-pressure-resistant alloys, welded joints, and high-pressure technique in general has made possible many reactions and the production of many compounds that either could not have been made on a commercial scale, or were the result of more roundabout, more expensive, and less reliable methods. A number of highly specialized operations have necessitated the development of equipment peculiar to these industries.

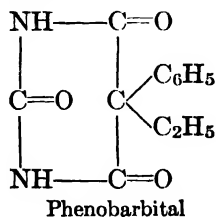
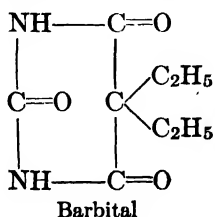
SYNTHETIC DRUGS

The earliest drugs were the dried and powdered bark, leaves, roots, and juices of plants, together with a few inorganic substances. Because of lack of uniformity in composition not one could be relied upon by physicians. Gradually methods of test and assay have been developed to a point where pharmaceuticals derived from plants are reasonably well standardized, and inorganic compounds are of a high degree of purity. With the beginnings of organic chemistry a century ago, the composition of the pure substances to which crude drugs owe their properties began to be found out. Along with this type of study, investigations of the physiological action of synthetic organic derivatives as well as inorganic compounds have been made. Among the earliest developments along this line was the use of chloroform and diethyl ether as inhalation anesthetics. Once the constitution of naturally occurring compounds such as cocaine, quinine, adrenaline, and hundreds of others became known, the synthetic organic chemist began to work on methods of synthesis of these substances. Many substances once obtainable in pure form only with great difficulty have now been synthesized; but what is still better, new compounds resembling them in structure have been made which have better physiological action. A great deal of the earlier work in the field of synthetic

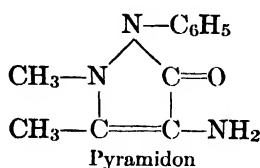
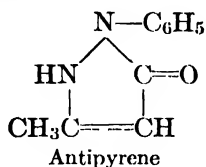
pharmaceuticals was purely of the nature of trial and error, tests being made on animals, and those compounds used clinically that showed the desired effects on test animals. On the basis of long experience some knowledge has been gained concerning the relation between chemical constitution and physiological action. Still another phase of this sort of work is the study of the chemistry of the cells, tissues, and solutions of the body, as well as the composition of bacteria, which play so important a part in animal life.

In the discussion which follows, attention will not be directed solely to synthetic aromatic derivatives, since carbon compounds of all sorts are used as pharmaceuticals. The following are some of the classes of compounds used in medicine, the classification being on the basis of physiological action rather than chemical constitution: general anesthetics, narcotics, and analgesics; local anesthetics; antiseptics; miscellaneous pharmaceuticals.

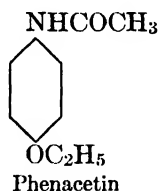
General Anesthetics, Narcotics, and Analgesics. The effect of these substances is to produce sleep, which may be so profound that the patient is insensible to pain, or merely sleep which is otherwise inhibited by nervous and mental conditions or minor irritation. In surgical operations, inhalation anesthetics are employed whose effects are realized very quickly and pass away in a very short time after administration ceases. Chief among these are chloroform, diethyl ether, and such substances as nitrous oxide and ethylene, which are administered along with oxygen. Divinyl ether, $\text{CH}_2=\text{CH}-\text{O}-\text{CH}=\text{CH}_2$, has recently been developed as an inhalation anesthetic. Since both ethylene and diethyl ether are anesthetics, it would be expected that this compound would function in the same way. The opium alkaloids, such as morphine, produce profound nervous depression, which means deadening of the sense of pain and even complete unconsciousness. They are extremely toxic and are also dangerously habit forming. Substances that produce natural sleep in patients who are not suffering intense pain are commonly known as hypnotics. The best known of these substances are cyclic ureides such as barbital and phenobarbital (formerly called luminal).



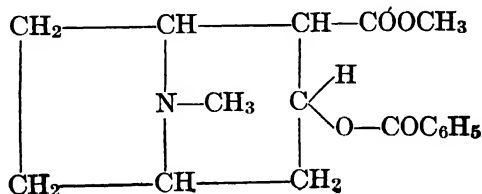
It is also possible to combine a hypnotic with a substance that relieves pain, known as an analgesic, and this is often necessary before sleep can be produced. Antipyretics are substances that reduce fever. Among the oldest of these is antipyrine, or phenylmethyl pyrazolone. By introducing another methyl group and an amino group, another substance called "pyramidon" is obtained, which is more effective and less dangerous.



Another febrifuge for a long time widely used but now being gradually discontinued is acetanilide, $\text{C}_6\text{H}_5\text{NHCOCH}_3$, which was called "anti-febrin." The most valuable drug of this nature possessing the power of relieving neuralgic pain and lowering body temperature is phenacetin.



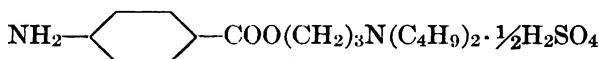
Local Anesthetics. These are compounds which produce insensibility to pain in a limited area or portion of the body, so that surgical operations may be carried out without the danger and the disagreeable after-effects of inhalation anesthetics. Though more largely used for minor operations and dental work, local anesthetics are increasingly used in connection with major operations. Somewhat akin to these substances are dusting powders, which relieve pain locally in ulcers and areas from which skin has been removed. The first generally used local anesthetic was the naturally occurring compound, cocaine, which has the formula:



Since it is not only toxic but habit forming, the organic chemist set out to synthesize compounds that would be more effective, less toxic, and less likely to produce a habit of using the drug. Those portions of the cocaine molecule that are effective were determined, and a number of substances were synthesized, among which two should be specially mentioned, procaine, a solution of which is used by injection, and butyn, which produces insensibility to pain both when injected and when applied to such surfaces as the eyeball or mucous membranes of nose and throat.

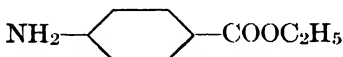


Procaine

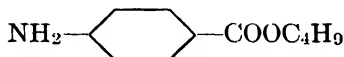


Butyn

Two substances are valuable in dusting powders and in ointments to produce deadening of pain in the nerves near the surface, anesthesin, *p*-aminoethyl benzoate, and butesin, *p*-amino-*n*-butyl benzoate.

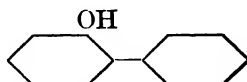


Anesthesin

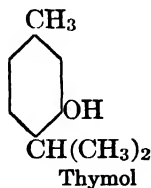


Butesin

Antiseptics. One of the earliest disinfectants and antiseptics ever used was phenol, $\text{C}_6\text{H}_5\text{OH}$. This substance is highly toxic and corrosive to animal tissue, and must be employed in great dilution. The higher phenols are less toxic and have greater bactericidal power, but being less soluble in water are commonly employed in the form of emulsions. Thymol, which may be prepared synthetically from *p*-cymene, has ten times the bactericidal power of phenol, and is used very extensively in tooth pastes and antiseptic lotions. It was once the main remedy for hookworm until displaced first by chenopodium and still later by carbon tetrachloride and tetrachlorethylene. Ortho-phenylphenol is said to have a phenol coefficient of 30 to 40, and to be particularly valuable as an antiseptic in the dairy industry, being practically non-toxic.

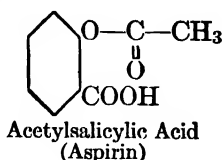


Ortho-phenylphenol



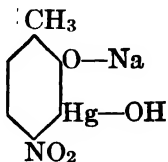
Thymol

Hexylresorcinol, $C_6H_3(OH)_2(C_6H_{13})$, developed as a result of studies on the synthesis and pharmacology of resorcinol derivatives, has the remarkable property of being fifty times as powerful a germicide as phenol and is so non-toxic that it can be administered by the mouth. The derivatives of salicylic acid, mainly esters, are administered internally. Aspirin, trade name for acetylsalicylic acid, has antiseptic properties, but is used largely to relieve headache and other pain and in the treatment of colds.

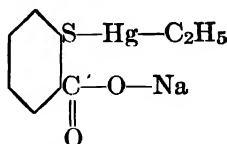


A number of organic dyes are used, both in the detection and diagnosis of disease and as antiseptics, among which may be mentioned methylene blue, gentian violet, and certain acridines and flavones. The power of bacteria to take up dyes selectively and become stained by them has been of inestimable value in bacteriology, and somewhat the same principles govern the chemotherapist's investigations.

Metallic compounds have long been used as disinfectants and germicides, particularly arsenic and mercury compounds. By including such elements in complex organic substances, the bactericidal power has been retained and the toxic and corrosive properties very greatly reduced. The following are notable examples of metal derivatives. Mercurochrome is the result of the combination of mercury and the synthetic aromatic dye, fluorescein. Neither alone could accomplish both results. Two very valuable and powerful mercurials have been developed in recent years, metaphen and merthiolate. Metaphen depends for its bactericidal power only in part on mercury, since nitro-*o*-cresol is a potent bactericide. It is also low in toxicity, and the mercury is not precipitated in the presence of serum and similar body fluids.



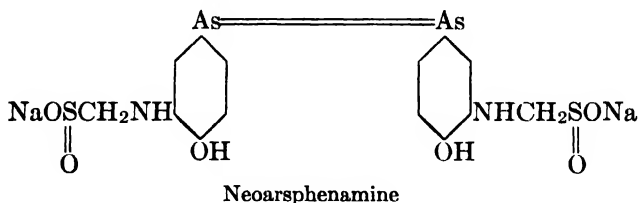
Metaphen



Merthiolate

Neoarsphenamine is an improvement on the original arsphenamine or "606," which lacked the sodium formaldehyde sulfoxalate group on the

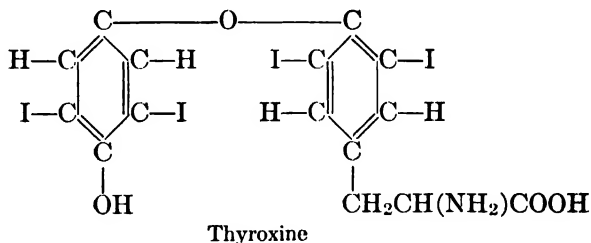
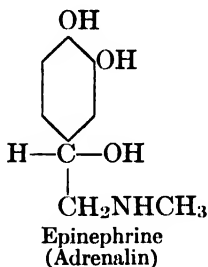
two amino groups. It is introduced directly in water solution into the veins, and has been widely used in the treatment of syphilis. Potassium bismuth tartrate and organobismuth compounds have to a very considerable extent replaced mercurials in the treatment of syphilis. Tryparsamide, $\text{NH}_2\text{COCH}_2\text{NHC}_6\text{H}_4\text{AsO}(\text{OH})_2$, is successfully used in paresis, a dangerous and usually fatal mental disease.



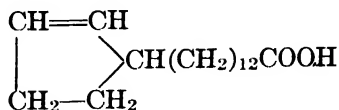
Miscellaneous Pharmaceuticals. A great many substances are used to act on the kidneys and gastrointestinal tract. Some of these are inorganic in their nature, such as mercurous chloride (calomel), sodium phosphate, magnesium phosphate, and many others are derived from plants and purified to a definite standard by the manufacturing pharmacist. There are also synthetic derivatives such as certain piperazine derivatives and hexamethylenetetramine, which are used for uric acid disorders, and the laxative, phenolphthalein.

A considerable number of hormones or chemical regulators, which have very powerful effects even in exceedingly minute amounts, are produced in the body. Only two of these have been identified as single chemical individuals, but others have been obtained in relatively concentrated form from bodies of sheep and cattle at the packing houses, and are used with great success in the treatment of a variety of diseases. Among the later is insulin, which has finally been gotten in crystalline and highly potent form but whose chemical composition is not known. This product, generally used in the relief of diabetic patients, is made from certain cells of the pancreas of animals, and is standardized by its effect on the blood sugar of rabbits. The two hormones whose constitution is known and which have been successfully synthesized are epinephrine (adrenalin) and thyroxine. Epinephrine is produced by certain glands above the kidney. This substance was isolated in pure form and its constitution determined several years ago, and methods of synthesis have been worked out. Since only a few hundred pounds of it are used in a year and its synthesis requires the greatest skill and involves the isolation of one optically active isomer from a racemic compound, it is still produced commercially

from the glands of animals that are slaughtered for food. It has most varied and extensive effects, such as increase of arterial blood pressure, very pronounced change in the rate and manner of respiration, relaxation of certain parts of the body and constriction in others, and increase in the formation of blood sugar from glycogen. It is used in connection with local anesthetics to prevent too rapid diffusion of the anesthetic, in surgery to check surface bleeding, as a life-saving measure in case of sudden collapse, to increase the sugar content of the blood when an overdose of insulin has been administered, in relieving serum sickness due to hypersensitivity, and particularly to produce normal breathing in bronchial asthma. Thyroxine has been synthesized, but is made commercially from the thyroid glands of hogs. It is used in the treatment of individuals suffering from disturbances of the functions of the thyroid gland. The effect of this organic iodine derivative is considered to be catalytic. Insufficiency of thyroid secretion leads to goiter, to myxedema in adults, and to cretinism in children. Goiter may be prevented by small amounts of iodine in salt or in drinking water, but the treatment of these diseases requires thyroxine in pure form or as dried thyroid glands.



An example of a naturally occurring product that has been improved by conversion into other derivatives is chaulmoogra oil, which has been used very successfully in the treatment of leprosy in its earlier stages. The organic chemist has found the structure of chaulmoogric acid to be



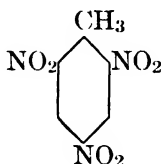
and has made esters of this acid from chaulmoogra oil that are more satisfactory and less unpleasant to the patient than the oil itself; on the basis of this knowledge some synthetic products of still greater value are likely to result.

The synthesis of pharmaceuticals is for the most part carried out on a relatively small scale, and requires considerable skill and the highest quality of analytical control. The matter of cost of material is secondary; the chief considerations are uniformity and purity rather than economics of chemical engineering. Not only are many of the raw materials derived from the by-products of coal distillation, but most of the unit processes by which pharmaceuticals are made and the type reactions employed are so similar to those characterizing the manufacture of synthetic aromatic derivatives that synthetic drugs may rightly be classed along with dyes and nitro-aromatic explosives as a distinct division of the chemical industry.

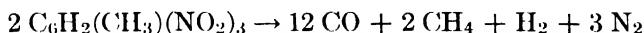
NITRO-AROMATIC EXPLOSIVES

A very important class of explosives, particularly those used in filling shell, mines, bombs, and depth charges for destruction of submarines, are nitro-aromatic derivatives. It should be understood that some of the substances discussed below are not made at all in peace times.

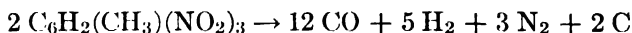
✓ **Trinitrotoluene, T.N.T.** This is a very powerful explosive, and is at the same time an extremely stable material. In its pure form, it melts at 80.82° C. without any sign of decomposition, hence it may be readily melted and poured into shell.



It is supposed to decompose under ideal conditions as follows:



but the actual reaction is probably more nearly this:

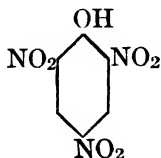


The toluene used for nitration must be quite pure, boiling from 108.5 to 112.5° C. In the single-stage process, mixed acid is slowly added to toluene with cooling, and the reaction mixture is warmed until reaction is complete. In the two-stage process, the mononitro derivative is made with spent acid from a previous run. The acid

is then removed, fresh acid added, and the trinitro compound made directly. The three-stage process employs spent acid from the making of dinitrotoluene, the product of the first nitration being "mono oil." This is transferred to another nitrator, and spent acid from the third stage is added. The dinitro derivative resulting from this treatment is separated from the acid and sent to the third nitrator, where it is mixed with fresh acid. This three-stage method was the one most commonly used in this country, although a few plants nitrated in one stage.

The product of any of these methods is cooled in lead-lined tanks, acid is drawn off from it, and the solid is again melted and mixed with an equal weight of sulfuric acid. The crystalline solid obtained on cooling this mixture is freed as far as possible from acid, melted, and washed with water until the washings are neutral. Water is removed by heating the molten material, after which it is allowed to crystallize. The yellow crystalline mass melting at 80°C. to 80.82°C. is soluble in most organic solvents and insoluble in water. When heated to 150°C. it begins to decompose, but it may be heated at this temperature for many hours without much effect. Its temperature of ignition depends somewhat on conditions, but is around 280°C. In the presence of alkalis it forms derivatives that are quite sensitive.

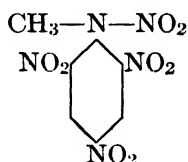
✓ **Picric Acid, Trinitrophenol.** Pure phenol, when mixed with a relatively small amount of sulfuric acid, gives as a product a monosulfonic acid. This is taken up with more sulfuric acid and mixed with nitric acid. The mixture, after being heated for 5 hours to 115°C. , is diluted, the spent acid drawn off, and the solid thoroughly washed and centrifuged. Another method consists in chlorinating benzene to monochlorobenzene, nitrating this to the chlorodinitrobenzene, hydrolyzing this compound to dinitrophenol by the use of alkali, freeing the phenol from its salt, and nitrating further with mixed acid to picric acid. Picric acid, when ignited, burns slowly without explosion. If the heating is rapid, detonation results. Picric acid itself is quite stable, but it forms sensitive picrates with most metals. Hence the shell in which it is used must have enameled or varnished linings. It is also used extensively as a dye and as an antiseptic.



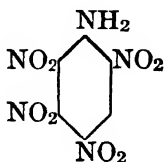
Ammonium Picrate. The ammonium salt of picric acid is very insensitive to detonation. It is produced by neutralizing picric acid with ammonium hydroxide, crystallizing, drying, and screening the resulting product. Ammonium picrate is loaded into shell by ramming, and if removed and reloaded it is found to be more sensitive to shock than freshly prepared material. This is probably due to being crushed and entrapping air on the first loading, which is heated by pressure on the second loading.

Waste picric acid and material contaminated so as to be unfit for use in shell were used during the war in making nitrochloroform, or "chlorpicrin," for use in gas shell, this material being a powerful lachrymator.

Tetryl (Trinitrophenylmethylnitramine). This material is used primarily as a booster explosive, or the intermediate charge which transmits detonation from the detonator to the bursting charge in high explosive shell, bombs, etc., and is a violent explosive. Aniline is first converted to dimethylaniline, the iodine used as a catalyst being recovered and used repeatedly. The dimethylaniline is first sulfonated and then treated with mixed acid.



T.N.A., Tetranitraniline. This substance was developed during the World War for use in detonators and booster charges; a plant was erected for its manufacture, but was never operated. It is a neutral and non-hygroscopic substance. It decomposes very slowly in the presence of moisture, being hydrolyzed to trinitroaminophenol. In the form in which it is used it is a solid melting from 208° C. to 215° C. It is made from dinitrobenzene, this being first converted to *m*-nitraniline by sodium sulfide. The purified *m*-nitraniline is mixed with nitric acid and kept cold for 12 hours, after which it is slowly heated until the temperature reaches 70° C.



T.N.X., Trinitroxylene. This substance was used to some extent in mines during the World War, but is not manufactured at the present time. It resembles T.N.T. very closely.

Amatol. A mixture of ammonium nitrate and T.N.T. is known as "amatol." The mixture most easily loaded into shell by casting contains equal amounts of the two substances. The T.N.T. gives the initial impulse to the explosive. "80-20 amatol" cannot be loaded into shell by pouring, but is put into the shell by tamping, pressing, or extruding processes. Theoretically, this is the best mixture, since it is close to the proportions for ideal combustion. It also gives larger gas volumes, hence greater "crater" effect. The 50-50 mixture gives better fragmentation in shell.

SYNTHETIC DYES

A dye is the term applied to substances that impart permanent color to such materials as fabrics, paper, and leather. Dyes are also used as tints in paints and stains, and after being adsorbed by white pigments constitute "lakes" or "dry colors." There are a few substances, such as lead chromate (chrome yellow), basic chromium oxide (chrome green), and ferric oxide (iron buff), which are entirely inorganic in their nature. There are also a number of dyes of natural origin, chief among these being logwood and fustic. Both of these are extracts derived from woods. At one time indigo was obtained entirely from a plant grown in the tropics, but the greater part of all indigo now on the market is synthetic. Probably less than 10% of all dyes used in the United States are of natural origin.

The synthetic dyestuffs industry has been developed in the United States practically wholly since 1914. Up to that time most dyes were imported, largely from Germany, and the few that were made in this country were assembled from imported intermediates. In 1929 the production of dyes in the United States amounted to 111.5 million pounds, and only 6.4 million pounds were imported.

Intermediates. The meaning of the term "crude" has already been explained. In making a dye all derivatives from the original crude to the finished dye are known as "intermediates." For the most part these substances are not colored, and even colored intermediates rarely have the power of imparting permanent color to other substances. Occasionally substances which may be used as dyes are further modified by chemical change to yield other dyes. Phenol from coal tar is a crude, but synthetic phenol from benzene is an intermediate.

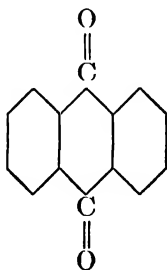
The most difficult part of the making of a dye lies in preparing

the necessary intermediates. Shreve has this to say regarding intermediates:

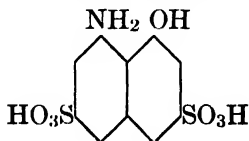
A correct valuation of the dye industry can only be had by a most thorough study and understanding of the intermediates. In four out of five instances not only the purity but also the cost of producing the finished product is absolutely dependent upon the quality and cost of intermediates. Furthermore, in the majority of cases, more chemistry and engineering is involved in the manufacture of intermediates than in that of dyes. Among the factors which cause the gap between laboratory and successful plant production are: details such as the speed of revolution of the mixing vats; the great importance of the materials out of which the equipment is constructed; the tremendous and often cumulative effect of impurities in the materials used; the personal equation of the workman; and the fact that reactions on a large scale are sometimes more difficult to control.

The several hundred intermediates are largely derivatives of benzene, naphthalene, and anthracene, and are for the most part amino, hydroxy, and sulfonic acid compounds. The three most important dye intermediates in terms of quantity produced are beta-naphthol, nitrobenzene, and aniline. The last two should be considered together, since nitrobenzene is made into aniline before being used in the synthesis of dyes. Not more than fifteen or twenty others are made in quantities exceeding one million pounds per year. It should be remembered that some intermediates are made from others, and that some very important and expensive dyes are made in relatively small quantities. A few typical and important intermediates, in addition to the three cited above, are:

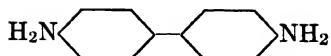
Anthraquinone:



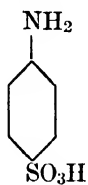
H Acid (8-Amino-1-naphthol-3 : 6-disulfonic acid):



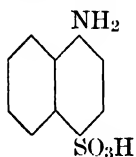
Benzidine:



Sulfanilic Acid (*p*-Aminobenzenesulfonic acid):

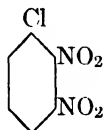


Naphthionic Acid (1-Aminonaphthalene-4-sulfonic acid):



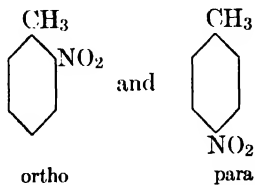
Chlorobenzene: C_6H_5Cl

1-Chloro-2 : 3-dinitrobenzene:

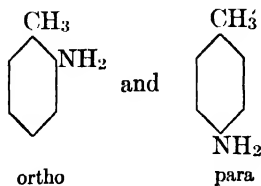


Dimethylaniline: $C_6H_5N(CH_3)_2$

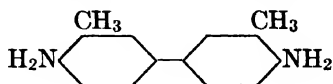
Nitrotoluene:



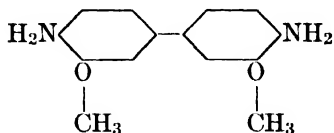
Toluidine:



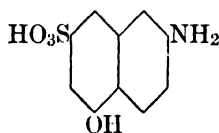
Tolidine (4, 4'-Diamino-3, 3'-dimethyl-diphenyl):



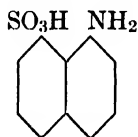
Dianisidine:



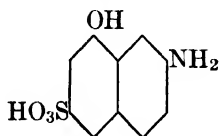
J Acid (2-Amino-5-naphthol-7-sulfonic acid):



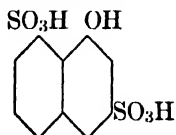
Peri Acid (1-Naphthylamine-8-sulfonic acid):



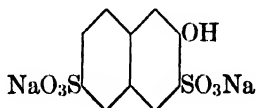
Gamma Acid (2-Amino-8-naphthol-6-sulfonic acid):



Epsilon Acid (1-Naphthol-3 : 8-disulfonic acid):



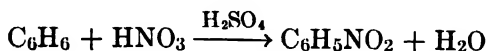
R-Salt (Sodium salt of 2-Naphthol-3 : 6-disulfonic acid):



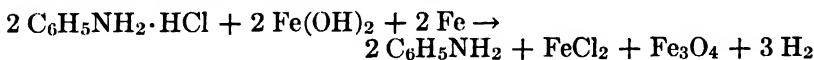
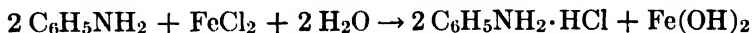
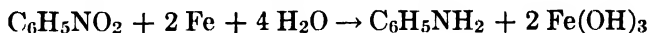
Phenol is used to some extent as a dye intermediate, but its greatest use is in the production of synthetic resins.

The synthesis of a few intermediates given below will serve to show in a general way the nature of intermediate manufacture.

Aniline. Nitrobenzene is first prepared by the action of mixed acid on benzene:



A mixed acid of the composition: sulfuric acid 60%, nitric acid 32%, water 8%, is used with about twice as much mixed acid by weight as benzene. There are various procedures in this nitration. Spent acid from a previous nitration may be put in first; to this is added the entire charge of benzene with cooling to 75° F., and the nitrating acid is slowly added with thorough stirring. Using a special type of nitrator it is possible to withdraw the original spent acid as rapidly as fresh mixed acid is put in so that the volume remains constant. Any nitrobenzene carried out with this acid is put back in a succeeding run. The nitrobenzene is freed from waste acid by settling, and is washed with water, with alkaline solutions, and finally with water containing a little aniline. The reduction of nitrobenzene is accomplished primarily by iron turnings in the presence of water containing hydrochloric acid in small amounts. In the more modern plants, no hydrochloric acid is added as such, but ferrous chloride to the extent of about 2% of the weight of the iron is put in. The probable reactions have been summed up by Groggins as follows:



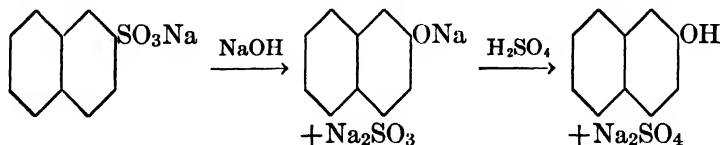
Thus the ferrous chloride appears to function as a catalyst. The ferric hydroxide is also reduced by iron to ferrous hydroxide. A certain amount of hydrogen is always formed, but the reduction is not simply a matter of generation of hydrogen by the action of acid on iron. The sludge which remains is primarily hydrated magnetic oxide of iron. The iron turnings or borings are added at intervals, and the reaction is carried out with temperature control but at a sufficiently high temperature so that there is continuous refluxing. The aniline is removed by decantation and steam distillation and purified by vacuum distillation. This substance is very toxic, and special precau-

tions must be observed in the way of ventilation, proper clothing, and medical examination of workers.

Beta-naphthol. The crude used in this case is naphthalene. Equal weights of 93% sulfuric acid and naphthalene are heated together at 160° C. to 165° C. for several hours. During the operation a small part of the naphthalene volatilizes and is recovered. The reaction results in the formation of both alpha- and beta-naphthalenesulfonic acids. The ratio of the two is about 15:85. Alpha-naphthalenesulfonic acid hydrolyzes more readily under the conditions of the process than the beta derivative, and by blowing steam through the reaction mixture it may be largely broken up into naphthalene and sulfuric acid without very much loss of the beta acid. The naphthalene is condensed and recovered.

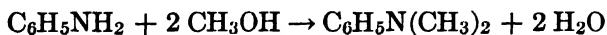
Beta-naphthalenesulfonic acid is converted to the sodium salt by the addition of a solution of sodium sulfite, which is a by-product of the later fusion reactions. Sodium chloride is also added to secure the desired specific gravity of solution to bring about proper separation. The sodium salt is recovered by filtration. An alternative method of separating the alpha and beta compounds, which is now used comparatively little, is to neutralize the mixture of sulfonic acids with calcium carbonate. The calcium salt of the alpha acid is soluble, and that of the beta acid is insoluble. Sodium carbonate or sodium sulfate acting on a suspension of the beta compound produces the sodium salt.

The sodium salt of beta-naphthalenesulfonic acid is fused with caustic soda for several hours, the fused mass quenched in water, and the solution clarified by filtration. Acidification with sulfuric acid frees beta-naphthol, which is washed several times with boiling water.



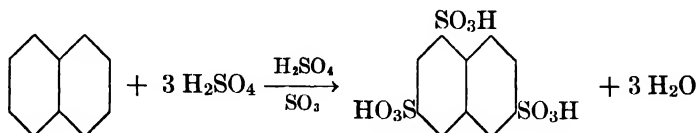
The beta-naphthol is distilled under reduced pressure. This process is said to give yields of about 65% on the basis of the naphthalene sulfonated.

Dimethylaniline. Aniline and methyl alcohol are heated together in an autoclave in the presence of a catalyst such as sulfuric acid. Pressures of 30 atmospheres are reached.

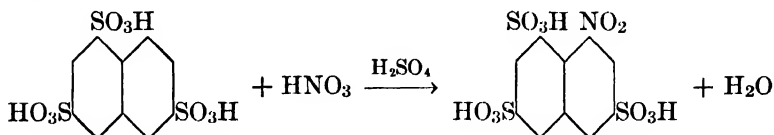


The acid is neutralized by caustic soda; unchanged methyl alcohol is removed by fractional distillation, and the dimethylaniline by steam distillation. The product is an oily liquid. This process is illustrative of alkylation.

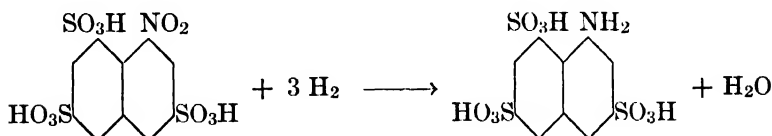
II Acid (8-Amino-1-naphthol-3:6-disulfonic acid). Naphthalene is sulfonated to the 3:6:8 trisulfonic acid.



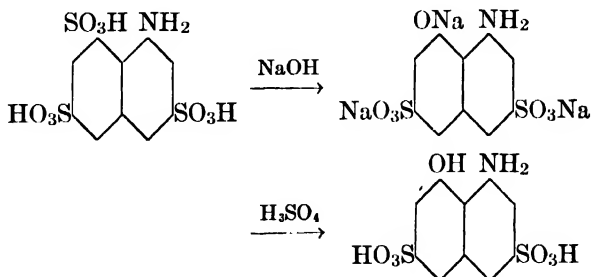
This compound is nitrated with careful cooling by the use of mixed acid.



The nitro derivative is reduced with iron and hydrochloric acid.



The resulting compound, known as "Koch's Acid," is 1-naphthylamine-3:6:8-trisulfonic acid. This in turn is fused with caustic soda, and the resulting sodium salt is treated with acid to obtain H Acid or its acid sodium salt.

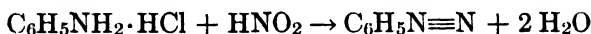


This not only illustrates sulfonation, nitration, reduction, and caustic fusion, but also shows the complexity possible in intermediate manufacture.

Dyes. Dyes contain certain characteristic groups that are often referred to as "chromophores." Among these are the nitro group, NO_2 ; the azo group, $-\text{N}=\text{N}-$; and the quinoid chromophore $=\langle \text{benzene ring} \rangle=$. Knowing the characteristics of one rather simple dye, chemists are able to predict the change in color and other properties that will be brought about by the addition of other groups.

The actual making of a dye is the final step in a series of organic reactions, and is usually accomplished in a very simple manner and with very simple apparatus. Some of these substances will appear to be extremely complex. However, some of these molecules of apparent complexity can be very easily built up by the combination of simple intermediates. The expert dye chemist sees in the structural formula of a dye the units of the intermediates from which the substance is constructed, just as the architect sees in a building the units of beams, girders, and piers. A dye is often obtained as a filterable precipitate by the addition of sodium chloride to its solution or more commonly its colloidal suspension. This is known as "salting out." A few examples will be given as typical.

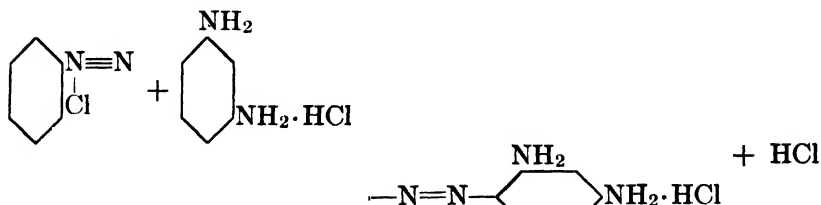
(a) *Azo Dyes.* The essential features of the production of azo dyes is the formation of a diazonium compound from one intermediate, and the coupling of this with another intermediate. When an aromatic amine in acid solution reacts with an equivalent amount of nitrous acid, the reaction mixture being kept cold, a diazonium salt results.



Aniline Hydrochloride
(Intermediate)

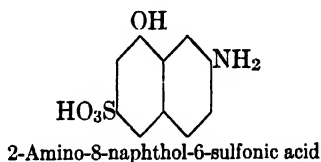
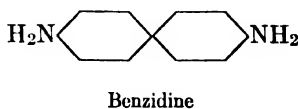
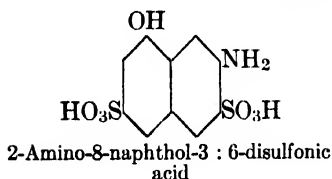
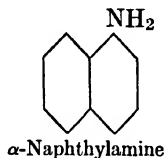
Cl
Benzenediazonium Chloride
(Never isolated in practice)

The diazonium chloride couples with various aromatic amines and phenols. For example, benzene diazonium chloride would couple with metaphenylene diamine hydrochloride thus:



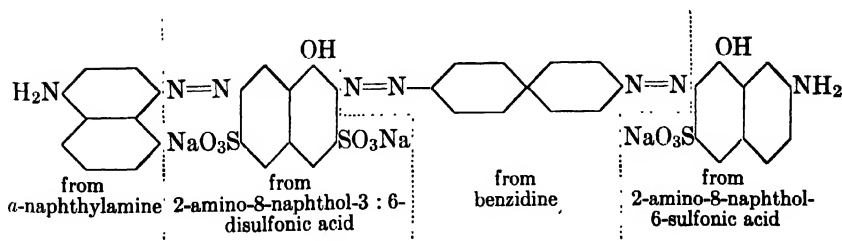
A more complex substance known as Direct Black V is made as follows. The sodium salt of 2-amino-8-naphthol-3:6-disulfonic acid

is diazotized and mixed with cooled alpha-naphthylamine and hydrochloric acid. The product, which is itself a dye, is dissolved in sodium hydroxide solution, and to this is added diazotized benzidine. To a suspension of this compound is added a solution of 2-amino-8-naphthol-6-sulfonic acid to which sodium hydroxide has been added. The intermediates are:

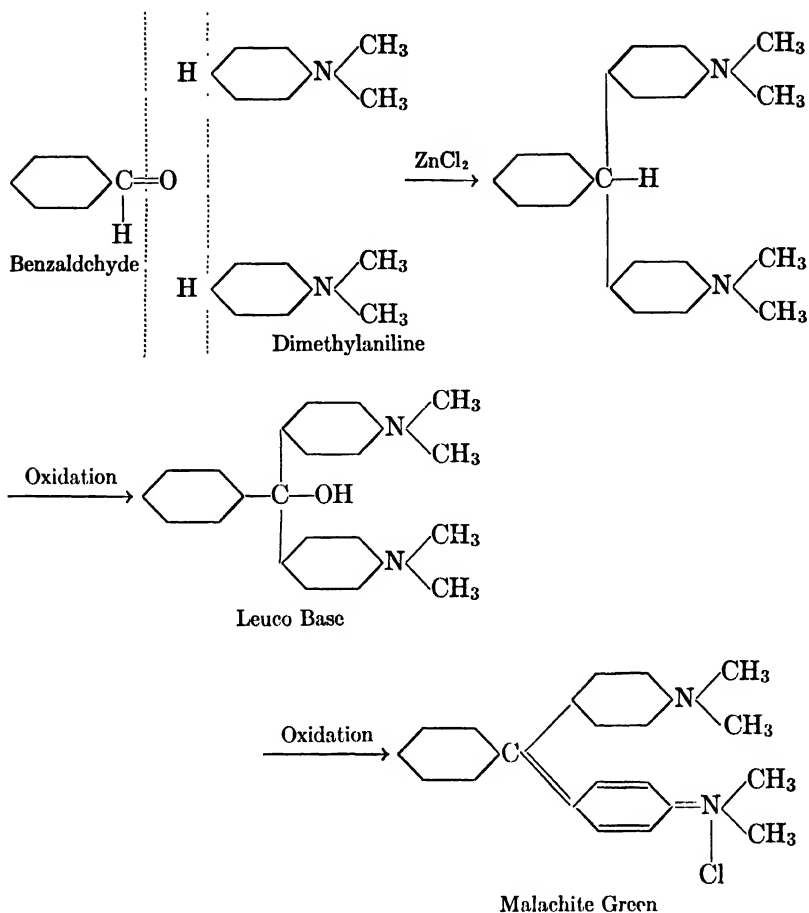


The final product has the formula:

DIRECT BLACK V

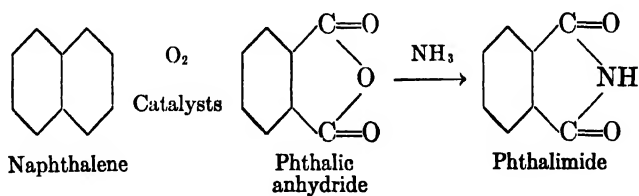


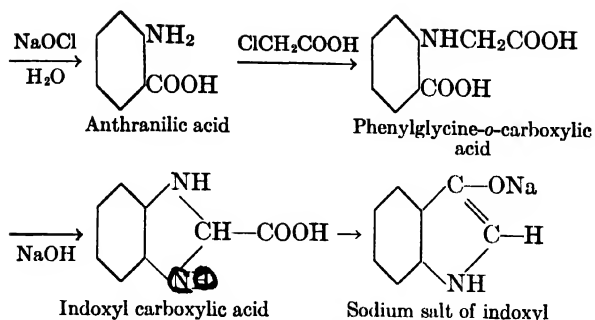
(b) *Triphenyl Methane Dyes.* A very important reaction is the removal of the elements of water from one mol of an aromatic aldehyde and two mols of an aromatic amine or phenol. The steps involved are as follows:



(c) *Indigo*. Two syntheses of indigo are given below, one of which uses naphthalene as a starting substance, the other aniline. The second synthesis is the one most commonly used now, the first being largely of historical interest since it was the first commercially successful process.

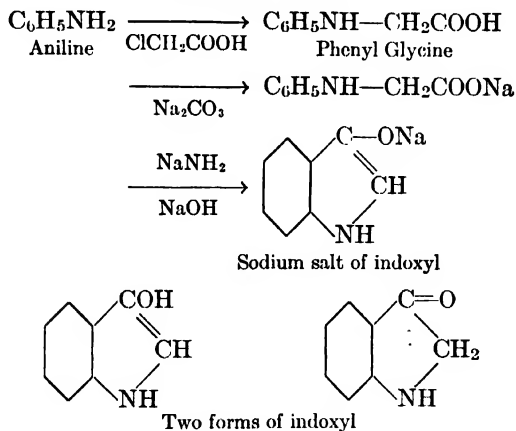
SYNTHESIS No. 1



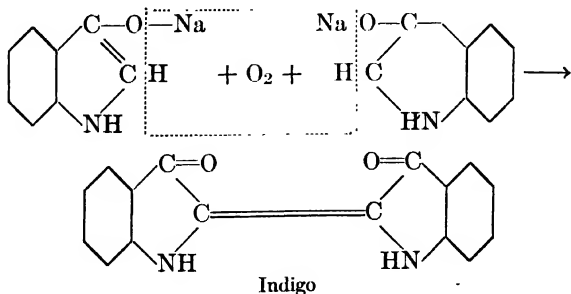


Before converting this to indigo, the second synthesis will be taken up and brought to the same point.

SYNTHESIS No. 2.



The oxidation of the sodium salt of indoxyl produces indigo and sodium hydroxide, atmospheric oxygen being employed.

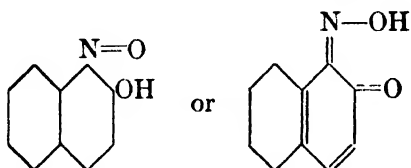


Classification of Dyes. For many years the classification of dye-stuffs generally used was that of Gustav Schultz in his monumental text "Farbstofftabellen." In 1924 the Society of Dyers and Colourists published their Colour Index, edited by F. M. Rowe, which is the classification now very generally used in England and the United States. The Colour Index lists all dyes under twenty-six heads, and each dye has a number. The same dye has a number of names depending on the firm making it, and all the names are listed together with the scientific name of the dye, its formula if the formula is known, the main components of the dye, the common methods of manufacture, and literature and patent references. Very much the same things characterize the Schultz text except that the classification is slightly different, and only eighteen groups are given.

For purposes of illustration the Colour Index classification is given together with a typical dye in each group. The total number of dyes listed in each group is given, together with the number of the dye used as an illustration, its scientific name, and a very brief statement of one method of manufacture.

I (1-6) Nitroso (Quinone Oximes).

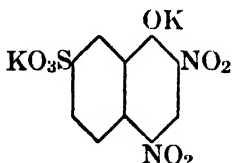
2, Naphthol Green Y. (α -nitroso- β -naphthol)
or 1 : 2-naphthaquinone-1-oxime



Made by the action of nitrous acid on beta-naphthol.

II (7-14) Nitro.

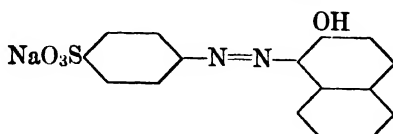
10, Naphthol Yellow.
(Potassium or sodium salt of 2 : 4-dinitro- α -naphthol-7-sulfonic acid.)



Made by the action of nitric acid on α -naphthol-2 : 4 : 7-trisulfonic acid.

III (15-229) Mono-azo.

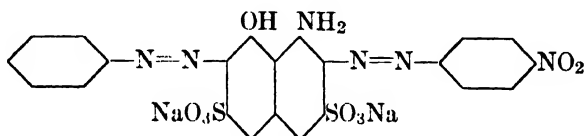
151, Orange II.

(Sodium salt of *p*-sulfo benzene-azo- β -naphthol.)

Made by coupling diazotized sulfanilic acid with beta-naphthol.

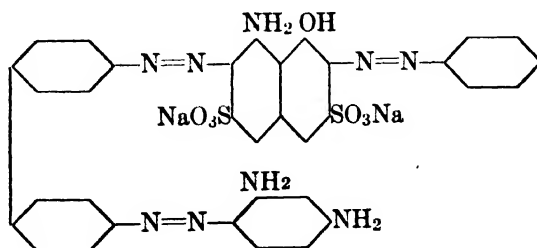
IV (230-530) Dis-azo (Primary, Secondary, Tertiary, and from Amines).

246, Naphthol Blue Black.

(Sodium salt of *p*-nitro benzene-azo-3 : 6-disulfo-1-amino-8-naphthol-azo-benzene.)Made by coupling diazotized *p*-nitroaniline with 1-amino-8-naphthol-3 : 6-disulfonic acid, and then coupling with diazotized aniline.

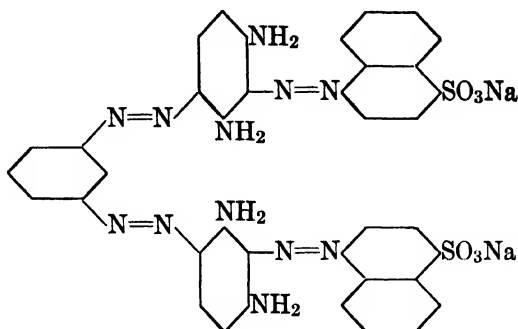
V (531-605) Tris-azo.

581, Direct Black.

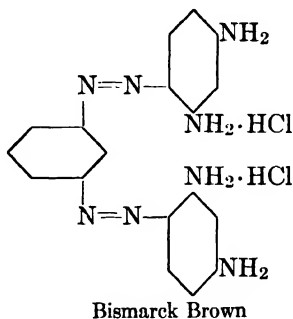
(Sodium salt of benzene-azo-3 : 6-disulfo-8-amino-1-naphthol-7-azo-diphenyl-azo-*m*-phenylenediamine.)Made by coupling tetrazotized benzidine with 1-amino-8-naphthol-3 : 6-disulfonic acid, then coupling diazobenzene chloride, and finally coupling with *m*-phenylenediamine.

VI (606-619) Tetrakisazo.

608, Direct Brown RB.

(Sodium salt of benzene-*m*-disazo-bis-*m*-phenylenediamine-disazo-bis- α -naphthalene-4-sulfonic acid.)

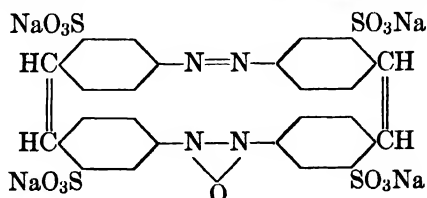
Made by coupling 2 mols of diazotized α -naphthylamine-4-sulfonic acid with 1 mol of Bismarck Brown.



VII (620-635) Stilbene.

620, Stilbene Yellow (Direct Yellow R).

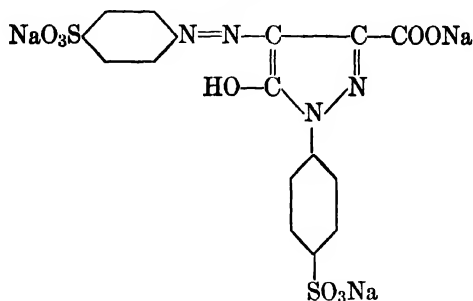
(Sodium salt of azoxy-azo-distilbene tetrasulfonic acid.)



Made by heating *p*-nitrotoluene-*o*-sulfonic acid with NaOH solution. Some material is formed that is not a dye together with a mixture of dyes of which the accompanying formula is typical.

VIII (636-654) Pyrazolone (Hydroxy-pyrazol).

640, Tartrazine.

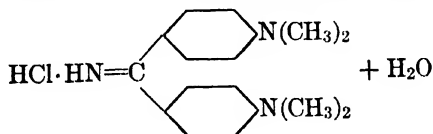
(Sodium salt of 4-*p*-sulfo benzene-azo-1-*p*-sulfo phenyl-5-hydroxy-pyrazol-3-carboxylic acid.)

Made by the action of 2 mols of phenyl hydrazine-*p*-sulfonic acid on 1 mol dioxytartaric acid.

IX (655-656) Ketonimine.

655, Auramine.

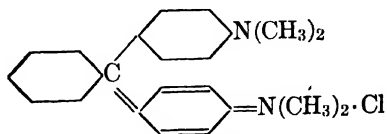
(Hydrochloride of Tetramethyldiamino-diphenyl-ketonimine.)



Made by heating tetramethyldiamino-diphenylmethane with sulfur, salt, and ammonium chloride in the presence of ammonia under pressure.

X (657-738) Triphenylmethane and Diphenylnaphthylmethane.

657, Malachite Green.

(Zinc double chloride or oxalate of *pp'*-tetramethyldiamino-triphenyl carbinol anhydride.)

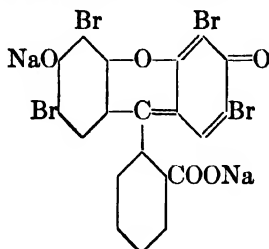
Formula of the hydrochloride

Made by condensing benzaldehyde with dimethylaniline in the presence of HCl to *pp'*-tetramethyldiaminotriphenylmethane, which is then oxidized with lead peroxide and acid.

XI (739-784) Xanthene.

768, Eosine.

(Sodium or potassium salt of tetrabromfluorescein.)

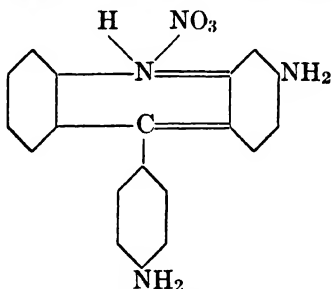


Made by brominating fluorescein.

XII (785-799) Acridine.

793, Phosphine.

(Mixture of the nitrates of chrysaniline, particularly chrysotoluidine.)



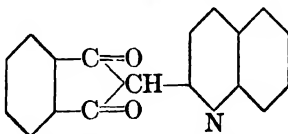
Formula of chrysaniline nitrate

Made by condensation of *p*-aminobenzaldehyde with *m*-aminodiphenylamine and oxidation of the product.

XIII (800-811) Quinoline.

801, Quinoline Yellow.

(Sodium salt of a mixture of the mono and disulfonic acids of quinophthalone.)



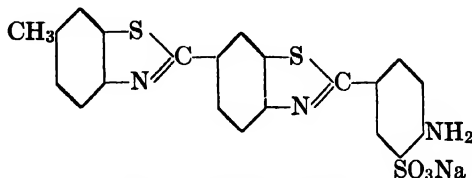
Formula of Quinophthalone

Made by condensation of 2-methylquinoline with phthalic anhydride in the presence of zinc chloride, and sulfonation of the product. The position of the sulfonic acid groups is not definitely known.

XIV (812-817) Thiazole.

812, Primuline.

(Mixture of the sodium salts of the monosulfonic acids of the more highly thionated dehydro-*p*-toluidine derivatives together with some dehydro-*p*-toluidine mono-sulfonic acid.)



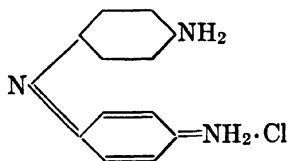
Formula of main component

Made by heating 2 mols of *p*-toluidine with 4.5 mols of sulfur and sulfonating the product.

XV (818-820) Indamine.

818, Phenylene Blue.

(Hydrochloride of *p*-aminophenyl-*p*-benzoquinone-di-imine.)

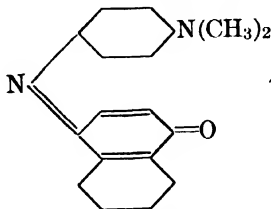


Made by oxidation of a mixture of equimolecular amounts of *p*-phenylenediamine and aniline hydrochloride with dichromate. These dyes are of no commercial importance in the United States.

XVI (821-823) Indophenol.

821, Indophenol.

(*p*-Dimethylaminophenyl- α -naphthoquinone-imine.)



Made by the action of *p*-nitrosodimethylaniline hydrochloride on alpha-naphthol.

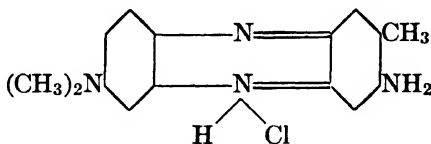
XVII (824-869) Azine.

864, Nigrosine (Spirit Soluble).

(No formula.)

Made by heating nitrobenzene, aniline, and aniline hydrochloride with iron or copper.

A simpler dye in this classification is 825, Neutral Red, which is made by the action of *p*-nitrosodimethylaniline hydrochloride on *m*-toluylene-diamine and heating the Toluylene Blue which is first obtained.



Formula of Neutral Red

XVIII (870-875) Aniline Blacks.

870, Aniline Black.

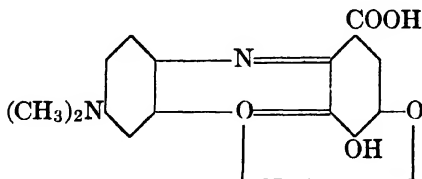
(No formula.)

Made by oxidation upon the fiber of aniline hydrochloride with a great variety of oxidizing agents including chlorates, copper salts, ferricyanides and chromates, and also atmospheric oxygen in the presence of catalysts such as *p*-phenylenediamine or vanadium salts. (Formulas have been written for aniline black, but they are pure guesses and are not worth the space they occupy.)

XIX (876-919) Oxazine.

883, Gallocyanine.

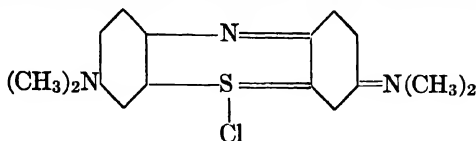
(Dimethylamino-hydroxy-carboxy-diphenoxazone.)



Made by the action of an excess of *p*-nitrosodimethylaniline hydrochloride on gallic acid in methyl alcohol solution.

XX (920-932) Thiazine.

922, Methylene Blue.
(Tetramethyldiamino-diphenaz-thionium chloride, zinc double chloride.)



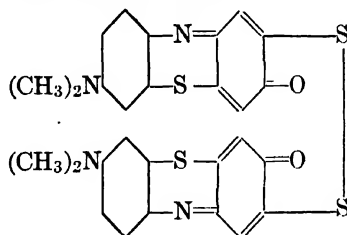
Made by the oxidation of dimethyl-*p*-phenylenediamine with dichromate in the presence of thiosulfate. The product formed and dimethylaniline are oxidized with dichromate and the indamine formed is converted into the leuco compound by dilute acid or zinc chloride. This is oxidized by dichromate and converted to the zinc double chloride.

XXI (933-1012) Sulfide (or Sulfur).

985, Sulfur Black.
(No formula.)

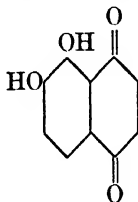
Made by heating a mixture of *m*-dinitrophenol and *p*-aminophenol sulfonic acid with sulfur and sodium sulfide.

Following is a guess as to the probable formula of a compound in in this class, 957, Thione Brilliant Blue.



XXII (1013-1026) Hydroxyketone, Hydroxyquinone, and Hydroxy-lactone.

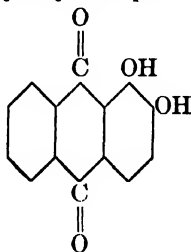
1019, Alizarine Blacks.
(7 : 8-Dihydroxy- α -naphthaquinone (Hydroxy-juglone, or its bisulfite.)



Made by the action of fuming sulfuric acid and sulfur on a mixture of 1 : 5- and 1 : 8-dinitronaphthalene and conversion to the bisulfite compound.

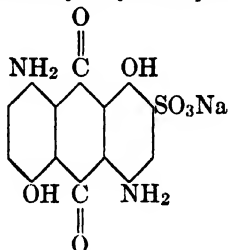
XXIII (1027-1093) Anthraquinone (Mordant and Acid).

1027, Alizarine (Mordant).
(1 : 2-Dihydroxyanthraquinone.)



Made by the action of various reagents on anthraquinone. A typical process is to heat anthraquinone with NaNO_3 and NaOH in the presence of Na_2SO_3 .

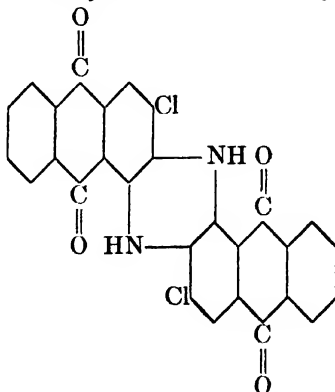
1053, Alizarine Blue, S.E. (Acid).
(Sodium salt of 4 : 8-diamino-1 : 5-dihydroxyanthraquinone-2-sulfonic acid.)



Made by reducing 4 : 8-diamino-1 : 5-dihydroxyanthraquinone-2 : 6-disulfonic acid and oxidizing the leuco base formed.

XXIV (1094-1175) Anthraquinone Vat.

1113, Alizanthrene Blue.
(3 : 3'-Dichloro-*N*-Dihydro-1 : 2 : 1' : 2'-anthraquinoneazine.)



Made by chlorinating *N*-dihydro-1 : 2 : 1' : 2'-anthraquinoneazine.

XXV (1176) Arylidoquinone.

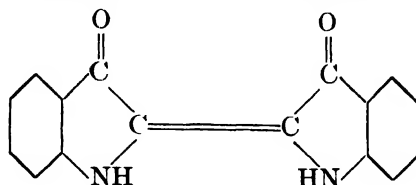
1176, Helidone Brown CR.

This dye is of no importance, and is not made in the United States.

XXVI (1177-1230) Indigoid.

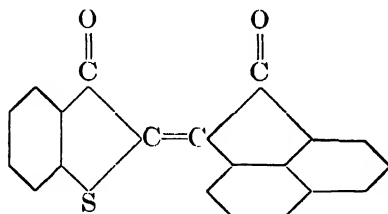
1177, Indigo.

(Indigotin or 2 : 2'-bis-indole-indigo.)



Made by the oxidation of indoxyl by the methods outlined earlier in the chapter.

1228, Ciba Scarlet (A typical thioindigo).
(2-Thionaphthen-2'-acetnaphthylene-indigo.)



Made by condensing acetnaphthenequinone, or its partial reduction product, with thioindoxyl or its carboxylic acid.

Several thousand dyes are made from several hundred intermediates, and these in turn are made from a dozen crudes. New dyes are being developed continually. A classification of dyes according to the intermediates from which they have been made has been compiled by Shreve. This is of great value to the manufacturer, since the first information desired about a dye is the intermediates from which it may be made. In this text, Shreve lists nearly 500 intermediates and 2500 dyes.

Application of Dyes. Wolfgang Ostwald has said:

We are not justified in speaking of a "theory of dyeing" as if any single theory can be applied to all processes of dyeing. Dyeing is not a scientific but a technical notion, which denotes uniform results without regard to the means employed. Science is bound to take into consideration the means, and if they are found to be different, it must put forward correspondingly different theories of the dyeing processes which depend on them.

The preponderance of evidence is in favor of regarding the phenomena of dyeing as colloidal in their nature. Glass, silica, asbestos, and similar inert materials in the form of fine fibers may be dyed. It is possible to extract dyes from fibers by means of proper solvents. The rate at which the dye is taken up by the fiber indicates colloidal adsorption.

Many dyes are shown by the ultramicroscope to be capable of forming colloidal solutions. Whether or not a dye will be adsorbed by a given fiber depends on the physical state and chemical constitution of the dye, and also on the general nature of the fiber. Many dyes will be adsorbed and held firmly by the fiber. Others require the use of a "mordant." This term refers to a substance that is precipitated on the fiber in colloidal form and strongly adsorbed by the fiber. In this condition the mordant adsorbs the dye. In other words, the fiber adsorbs the mordant and the mordant adsorbs the dye. The formation of insoluble products commonly called "lakes" or "color lakes" from dyes and alumina and other hydrous oxides may be regarded in most cases as an adsorption phenomenon. Some lakes can be made by simple grinding and make no pretence at being anything more than mechanical mixtures. There are true chemical compounds, generally calcium and barium salts of sulfonic acids of known composition, that are often called lakes, but the term "toner" is preferable for such compounds.

Classification of Dyes According to Use. The textile chemist is not greatly concerned with the derivation of a dye or its structural formula, but wishes to know the fibers with which it can be used, how it can be applied, what color and shade he can obtain, and the fastness of the dye towards light, soap solutions, and other solutions and solvents.

Matthews has divided coloring matters, with relatively few exceptions, on the basis of their general properties as follows:

Acid Dyes. Salts of color acids. Dye animal fibers directly. Do not dye vegetable fibers. Mostly applied to wool and silk.

Basic Dyes. Salts of color bases. Dye animal fibers directly. Dye vegetable fibers on a tannin mordant. Mainly used with cotton and silk.

Substantive Dyes. Of neutral chemical nature. Dye both animal and vegetable fibers directly. Mostly applied to cotton, and to some extent to wool and silk.

Mordant Dyes. Of neutral chemical nature. Dye neither animal nor vegetable fibers directly, but require a metallic mordant. Mostly applied to wool.

Sulfur Dyes. Soluble in sodium sulfide solutions. Used exclusively for vegetable fibers, which they dye directly. These dyes themselves contain sulfur.

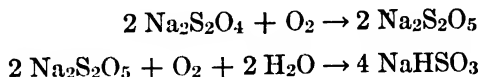
Vat Dyes. Soluble in sodium hydrosulfite. Dye both animal and vegetable fibers directly. Used mostly on cotton, and to some extent on wool. Characterized by great fastness.

Shreve lists all dyes under these headings:

Acid Dye.	Color Made on Fiber.
Acid Chrome Dye.	Mordant Dye.
Basic Dye.	Sulfur Dye.
Color Lake.	Spirit Soluble Dye.
Direct Dye.	Vat Dye.

"Direct dye" corresponds in general with "substantive dye" as defined above. "Acid Chrome Dye," sometimes called "after chrome," refers to a dye which is applied to a fiber in an acid bath and subsequently treated on the fiber by dichromates and chromium salts. "Color Made on Fiber" means that the dyestuff is actually produced from one constituent adsorbed on the fiber, by the addition of another constituent or reagent. These colors include: (a) "ingrain dyes" or "ice colors," which are made by impregnating ("padding") the cloth with sodium beta-naphtholate or similiar phenolates, and passing it through an ice-cooled bath of a diazotized amine; (b) "developed dyes," made by adding a dyestuff to the fiber, diazotizing one or more free amino groups, and coupling it with such a substance as beta-naphthol; (c) "coupled dyes," made by applying one dye to the fiber, and coupling it with another diazotized dye or intermediate to form a new dye. These are essentially variations of the same general process.

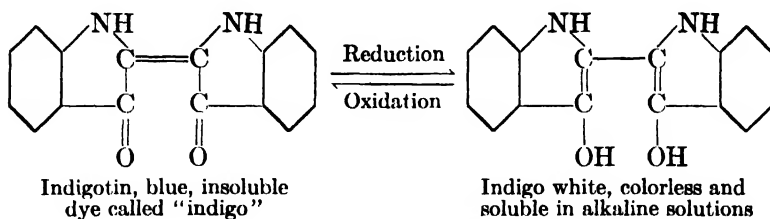
"Vat dyes" refer to insoluble color substances which can be readily converted to a soluble and usually colorless modification by the use of reducing agents. The methods of reduction include fermentation, zinc in alkaline solution, or sodium hydrosulfite, $\text{Na}_2\text{S}_2\text{O}_4$. Sodium hydrosulfite reacts readily with oxygen:



It is therefore a powerful and valuable reducing agent in the application of vat dyes.

The soluble derivatives of the dye having been thoroughly fixed on the fiber, the dye is developed by allowing the impregnated fiber to

dry in the air, slow oxidation taking place. Many valuable and permanent dyes belong to this classification, including the indigos, thioindigos, and various anthracene derivatives. The change of indigo to indigo white and its regeneration are indicated as follows:



"Mordants" are mainly basic in their nature, and include aluminum hydroxide, ferric hydroxide, chromium hydroxide, and stannic oxide. Acid mordants are represented largely by tannic acid in the form of an emulsoid sol, and sulfur in colloidal solution. Mordants may be still more firmly held on the fiber by the use of such reagents as antimony salts with tannic acid, and albumins, starches, and gums. The salt from which the mordant is derived, aluminum acetate for example, is called the "mordanting principle." The reagent which causes the formation of the colloidal mordant is called a "mordanting assistant." Silk and wool take up metallic mordants readily. Cotton must be wet with the solution of the mordanting principle, which is then very slowly hydrolyzed, after which products of hydrolysis other than the colloidal hydroxide are removed.

The composition of the dye bath varies greatly with the type of dye and the kind of cloth. Inorganic salts such as sodium acetate and sodium sulfate are extensively used in solution in the bath. They are known as "leveling agents." If the dye in colloidal solution is extremely finely divided and is adsorbed rapidly by the fiber, the coloring will be very uneven, that portion of the cloth going into the dye bath first receiving the larger part of the dye. The electrolyte serves to cause a partial coagulation of the colloidal matter and a precipitation of the colloid, and thus retards its adsorption. Silk glue in soap solution is a common dye bath ingredient, serving probably as a buffer to regulate hydrogen ion concentration of the bath. It is also possible that the proteins of the silk glue take up the dye first and then give it up slowly to the cloth. Temperature also controls the degree of dispersion of the dye material.

The matter of hydrogen ion concentration is important. Some

dyes are best applied in the presence of free acid. In regard to this Bancroft writes:

An anion is adsorbed more readily in the presence of readily adsorbed cation, and a cation in the presence of a readily adsorbed anion. In an acid dye the color is in the acid radical and in a basic dye in the basic radical. An acid dye will therefore be taken up more strongly in an acid solution than in a neutral solution, and will be taken up least in an alkaline solution. A readily adsorbed anion will decrease the amount of dye taken up, and a readily adsorbed cation will increase it. With a basic dye, the reverse will be true. . . . With substantive dyes the effects of electrolytes are different, and the question of stability enters in. *

The simplest method of applying a dye to a yarn or fabric is to immerse it intermittently by mechanical means in the dye bath. Dyes are often applied in the form of colored stripes or patterns. This is done by a printing process, a single engraved roll or cylinder being used for each color. The dye is often applied as a pigment in a paste of dextrin, in which case it acts directly, the dextrin being ultimately washed out. The cloth may have been previously treated with a mordant before printing. The cloth may be printed with one constituent and another added later after the fashion of ingrain dyes. The weaving of a pattern with threads of different colors requires very complex and expensive looms, known as "Jacquard Looms," and is confined to the finer grades of silks and woolsens.

SYNTHETIC RESINS

The topic of "Synthetic Resins" may be logically discussed in this chapter because two very important synthetic resins depend for their manufacture on synthetic aromatic derivatives. Phenol is the most widely used aromatic derivative in the synthetic resin field in the United States, and phthalic anhydride is increasing in importance.

The term "resin" refers to substances of varied chemical nature that possess certain physical properties such as amorphous structure, conchoidal fracture, brittleness, lustre, insolubility in water, and fusibility and plasticity when heated. The natural resins are secretions from trees and other plants. One of the best known is rosin, which is obtained as a residue after the distillation of the exudation of pine trees, the volatile material that is removed being "spirits of turpentine." The non-volatile residues that remain when fluid plant secretions are exposed to air for a few years are known as "recent resins." After several centuries have elapsed, the products of slow

* Quoted from "Applied Colloid Chemistry" by permission of The McGraw-Hill Book Co.

chemical change are known as "recent fossil resins." Materials that were thus formed so long ago that the time is measured in thousands of years are known as "fossil resins." These resins of various ages are for the most part polymerization products of terpenes, and are made up largely of resin acids, anhydrides, and esters. Resins and gums are distinguished from each other by the fact that gums are carbohydrates and are of recent origin.

Certain bituminous substances of the nature of asphalt and pitch have many of the physical properties of resins, and are probably the result of destructive and synthetic reactions caused by heat and pressure.

Synthetic resins are materials that have some of the properties of the vegetable resins, but differ in a number of respects, particularly in that many of them are infusible, insoluble, and extremely resistant to the action of a variety of chemicals. Since they are carbon compounds they can be burned; but instead of melting, the infusible types merely char at elevated temperatures. As the name implies, they are the products of synthetic organic reactions, and are made from compounds of known composition.

Two types of chemical change result in the formation of resins, polymerization and condensation. It is known that certain groups in organic compounds are characterized by readiness to polymerize. Among these may be mentioned the acetylene linkage $-C\equiv C-$, the ethylene linkage $>C=C<$, and systems of conjugated double bonds as in the butadienes. Condensation involves reaction between two or more molecules of the same compound, between molecules of different compounds, and between two groups in a single molecule, water, hydrogen sulfide, hydrogen halides, or hydrogen being removed. Some compounds undergo polymerization under one set of conditions and condensation under another. For example, acetaldehyde, C_2H_4O , polymerizes to form paraldehyde, $C_6H_{12}O_3$, and condenses to form crotonic aldehyde, $CH_3CH=CH-CHO$.

In the formation of resins there may be polymerization alone, as illustrated by the resinification of cumarone and indene. On the other hand, there may be condensation at the outset, as in the case of phenol and formaldehyde, followed by the polymerization of the products formed.

Synthetic resins may be broadly classified as (a) those that can be dissolved in suitable solvents and are permanently fusible, and (b) those that are at first fusible but under the influence of further heating become insoluble and infusible. The term "thermoplastic"

has been very generally applied to a synthetic resin to indicate that it is molded in a plastic state under the influence of heat and generally under the influence of pressure. The most important characteristic of synthetic resins of the second type is that they are "heat-setting," which means that they harden while hot. The ordinary fusible material of the resinous type can be molded hot and hardens as it cools. The infusible resins are the results of changes that take place during the molding period, a fusible and partially polymerized plastic substance being changed into a more completely polymerized, hard, infusible solid.

Fully six hundred trade names of synthetic resins have appeared, many referring to same material. Some of these names are obsolete, some of the resins are made only in small quantities, and only a few represent production in large amounts. Of those synthetic resins that are related to coal products some 33,000,000 lbs. were made in the United States in 1929. Of this quantity 26,000,000 lbs. were represented by the phenol-formaldehyde type, and 7,000,000 by the cumaron-indene resins and the glyceryl phthalate (Glyptal) resins. Large quantities of urea-formaldehyde and thiourea-formaldehyde resins are manufactured abroad, and their production is increasing in this country. The vinyl resins are also of commercial significance.

Phenol-Formaldehyde Resins. In 1872, Baeyer found that the reaction between phenols and aldehydes with the formation of resin was a general one, and a few years later Michael studied the action of benzaldehyde on various phenols. It was not until the beginning of the present century that the industrial possibilities of these resins were investigated. The principal technical difficulties were that soluble-fusible resins were more expensive than the natural resins and that the hardening of the insoluble-infusible resins could not be controlled, the material swelling and becoming porous before it hardened. The pioneer worker in this field, whose successful development of phenol-formaldehyde resins as materials of industrial use laid the foundation of the modern synthetic resins industry, was Dr. Leo H. Baekeland. All this work was done in the United States, and his results were publicly announced in 1909. The use of catalysts to control the reaction, the use of higher temperatures in molding than employed by earlier investigators, resulting in more rapid polymerization to the insoluble-infusible resin, and the use of pressure to avoid swelling and foaming, were characteristics of the process developed by Dr. Baekeland. The first products of this type were given the trade name Bakelite.

4. *Laminated Products.* The term "laminated" refers to materials made up of plates or thin layers. Linen, canvas, or paper are employed, depending on the nature of the desired product, a number of layers being impregnated with the resin in the A stage, and then subjected to heat and pressure. The resulting product in the form of sheets, tubes, and rods has many uses. As a material of construction in interior walls and furniture, the laminated product has many possibilities. Its chief use is in making "silent" gears.

5. *Bonding Agents.* Phenol-formaldehyde resins are extensively used as bonding agents, the chief uses being in sealing the glass bulbs of incandescent lamps to their metal sockets, and in making cutting and grinding wheels. In the latter case, the resin forms a very strong bond between the grains of abrasive. Since the resin merely dusts off along with the abrasive, there is not the power requirement of substances that fuse, flow, and are sticky. The statement has been made that granite is now cut as rapidly as limestone was a few years ago, and even though it takes more power to cut granite, the power consumption in this case is one-third what it was with fusible binders.

Phthalic Anhydride-Glycerin Resins (Glyptals). A number of the esterification products of polyhydric alcohols and polybasic acids form resins, but the principal materials used commercially are phthalic acid in the form of its anhydride and glycerin. It is obvious that there are various ways in which this esterification can take place. Phthalic anhydride and glycerin are heated together until they melt, and the temperature is maintained considerably above the melting point of the mixture until a product of the desired properties has been obtained. At a certain point in the polymerization the resin is fusible and soluble; longer heating results in an infusible and insoluble resin. In order to obtain a material that will give flexible films, castor oil and fatty acids such as oleic are often used along with phthalic anhydride in order to produce mixed esters. Glycol adipate and glycol succinate function as plasticizers for the cured resins.

The phthalic acid-glycerin resins are commonly known as "alkyd resins," and the softer varieties as "modified alkyd resins." These resins are remarkably opaque to ultraviolet light. They are miscible with nitrocellulose and soluble in nitrocellulose solvents. The modified alkyd resins are soluble in drying oils. These properties render such resins of great use in the field of protective coatings. When they are employed with nitrocellulose in lacquers, not only is it possible to have more solids present with the same viscosity of lacquer, but the lacquer

so made is remarkably resistant to disintegration by light and very waterproof.

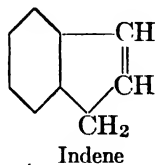
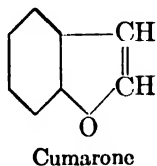
The insoluble glyceryl phthalate resins are somewhat slow curing, but have certain properties that make them invaluable in the electrical industry. In the making of commutators they have taken the place of shellac because of their greater heat resistance. Transparent products can be made, but the greatest value of the insoluble resins is in the impregnation of various insulating materials such as mica.

Urea-Formaldehyde and Thiourea-Formaldehyde Resins. Although neither urea nor thiourea is a synthetic aromatic compound, a study of synthetic resins would not be complete without a reference to resins made from these substances.

Urea and formaldehyde react to produce substances known as methylol ureas which polymerize to form resins. Thiourea and formaldehyde form compounds in which there is present the resinifying group —N=C=N— , and which may be represented as $(\text{R—N=C=N—R})_n$.

There is relatively little information concerning these resins outside of the patent literature. Considerable quantities are made in this country and still larger amounts abroad. The "Beetle" resins are urea derivatives, and are heat-hardening. Transparent and practically colorless products are made which are said to resist discoloration remarkably well. The molded products are quite tough, are capable of beautiful color effects, and are extensively used in drinking cups and tableware. These resins are undoubtedly of increasing importance.

Cumarone and Indene Resins. Cumarone and indene, as pointed out in a previous chapter, are important compounds of coal tar, and are present in the solvent naphtha obtained by fractionating the oils distilled from coal tar.



Both of these substances polymerize readily to resins in the presence of sulfuric acid. In order to offset the effect of the strongly exothermic reaction, these substances are not removed from the remaining components of the solvent naphtha but are treated with sulfuric acid in solution in a mixture of aromatic hydrocarbons. The amount of acid

is of the order of 10% of the weight of the polymerizable substances. The mixture is rapidly circulated and the temperature regulated by cooling coils. At the end of the operation, tar is allowed to settle, the residual acid is neutralized by soda, and the solution of resins thoroughly washed with water. The solvent, some naphthalene, and certain polymers of indene are removed by distillation. The resulting resins are of the fusible type, and are used mainly in the varnish industry.

Vinyl Resins. The group $\text{CH}_2=\text{CH}-$ is known as "vinyl." Halogen vinyl derivatives, styrol, $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$, and cyclanon vinyl compounds are the substances commonly employed in production of resins by polymerization. Products of this type are not so well known in this country as abroad. They are used mainly in molded articles, have some use in lacquers, either with or without nitrocellulose, but are rarely associated with drying oils in varnish products.

CHAPTER XXVI

EXPLOSIVES

The whole plan of this book has been to group substances by their chemical nature rather than by their industrial use. So far this plan has been followed very closely, but it has been found necessary in the interest of clearness to add some material in which classification is by use, and to include a brief review of some topics already discussed. The first chapter of this nature is on Explosives. In the discussion of cellulose derivatives, the manufacture of cellulose nitrate and its use in smokeless powder were given in some detail. Later, in the section on organic compounds made from aromatic hydrocarbons, several important nitroaromatic derivatives were described and their use as explosives discussed. In order that a complete picture of the whole field of explosives may be given, this brief chapter has been included.

Explosives have been defined as "substances that decompose suddenly and violently because of heat or shock into more stable substances, giving rise to great pressure of gas, which may be utilized for practical purposes." There are many substances that will explode, but those that can be utilized practically are limited to compounds whose decomposition can be controlled.

Explosives may be divided into two general classes according to their use—military explosives and industrial explosives. During the World War the production of military explosives constituted an enormous industry, but in peace times explosives are primarily used industrially in farming, mining, quarrying, and excavating. From the standpoint of military use, explosives are considered as belonging to these three groups: propellants, high explosives, and detonators. Very much the same classification may be made for industrial explosives, except that for propellants the term "low explosives" should be substituted.

Propellants and low explosives are those whose rates of burning are sufficiently slow to permit their use in propelling projectiles from small arms and cannon, and to bring about mechanical effects where large quantities of gas are to be generated but where intense shatter-

ing effects are not required. The rate of burning is of the order of a few hundred meters per second, so that the gas continues to be evolved as the projectile travels up the barrel of the weapon or as the earth or rock is moved from its original position. High explosives include those substances that decompose with great rapidity, a wave movement passing through the material at the rate of several thousand meters per second. Such explosives could not be used in weapons, but are used in shell. In industry, high explosives are valued because of their ability to exert a powerful disruptive or shattering action known as "brisance." Detonators are themselves high explosives, quite sensitive to heat and shock, which are used in small amounts to initiate reactions in much larger masses of less sensitive high explosives. Detonators develop their maximum energy on simple ignition.

PROPELLANTS AND LOW EXPLOSIVES

Black Powder. The earliest explosives recorded in history were of the same nature as what is now called "black powder," a mixture of sulfur, potassium nitrate, and charcoal. Until the middle of the past century, black powder was the sole military explosive. It produces large quantities of smoke, leaves a solid residuc, and does not have the power of modern explosives. Hence it now has only limited use in warfare. A typical black powder has the following composition:

Potassium nitrate	75%
Charcoal	15%
Sulfur	10%

The ingredients are pulverized separately in ball mills, which are grounded to prevent ignition by sparks, and mixed; after the addition of a small amount of water, the powder is reground in pan mills. These mills are equipped with remote control so that no one is in the building when the machinery is in operation. The ground material is pressed into cakes, which are subsequently broken, and the granular product is rolled in drums with graphite so that the grains are coated to eliminate friction.

Black blasting powder is commonly composed of sodium nitrate, 73%; charcoal, 16%; and sulfur, 11%. It is divided into grades according to grain sizes, which vary from $\frac{1}{16}$ in. to $\frac{1}{2}$ in. in diameter. This is much coarser material than black gunpowder.

Nitrocellulose Powders. The preparation of this type of explosive has been fully described in the chapter on Carbohydrate Industries in connection with the products of cellulose esters. By way of re-

minder, the process is as follows. The cellulose in the form of purified short-fiber cotton is nitrated; the product carefully stabilized by long boiling treatment; the water removed by alcohol while the cellulose nitrate is under heavy pressure; ether is added; and the plastic solid, with addition of stabilizers, is formed by extrusion, the grains being finally dried to uniform humidity.

Granulated Nitroglycerin Powders. The term "granulated nitroglycerin powder" refers to a material made up mainly of sodium nitrate and combustible material together with a small amount of nitroglycerin. The average composition of such powders is as follows:

Nitroglycerin	5%
Combustible material	35%
Sodium nitrate	60%

The combustible material consists of sulfur, coal, and resin. The nitrate and combustible materials are ground separately and mixed, and the mixture is warmed until the resin melts. While the material cools it is rubbed through a fine-mesh screen. This produces hard and porous grains. To this granular material the nitroglycerin is added, a part of it being absorbed and a part coating the grains. The powder requires detonation by the use of a dynamite priming cartridge, and its rate of detonation is more than twice that of black blasting powder.

HIGH EXPLOSIVES

Those organic compounds that function as high explosives fall into two classes, nitric acid esters of polyhydric alcohols, and nitroaromatic derivatives. Ammonium nitrate is the most important inorganic explosive, and its use is discussed in mixtures of other explosives. Perchlorates have a limited use. Liquid oxygen may be mixed with carbon and organic compounds, and the mixture used within a few minutes after preparation. Although it is claimed that liquid oxygen has the advantage of evaporating in a short time in case of failure to detonate, this advantage is more than offset by the hazard in handling the cartridges impregnated with liquid oxygen.

Nitric Acid Esters. Glycerin, ethylene glycol, and certain related compounds react with nitric acid in the presence of sulfuric acid to form esters that are powerful and efficient explosives. A typical operation for the production of nitroglycerin is as follows. A charge of 7000 lb. of mixed acid, consisting of 40% to 44% nitric acid and the remainder sulfuric acid, is placed in a nitrator. This piece of equip-

ment is a closed vessel of iron, equipped with cooling coils and agitating devices, which include both paddles and perforated compressed-air pipes. Glycerin to the amount of 1300 lb. is sprayed very slowly into the mixed acid, the contents of the nitrator being kept cool by water or brine circulated through closed coils. Lower temperatures facilitate separation of the final product from the mixed acids, hence it is common practice to employ calcium chloride brines that are quite cold. The temperature is usually between 2° C. and 7° C. At the end of the operation the contents of the nitrator are run into a separating tank, and when two layers are clearly formed, the spent mixed acid is drawn off from the bottom. Any nitroglycerin in this acid is decomposed by steam during the process of nitric acid recovery. The nitroglycerin is washed with water and stored under sodium carbonate solution. All nitrators and tanks are equipped with "drowning tanks" into which the mixture may be dumped in case the chemical reaction threatens to get out of control.

The fumes of nitroglycerin ordinarily produce violent headaches. Some individuals develop temporary immunity, a few appear to be naturally immune, and others never become immune to the effect of the fumes.

The term "nitroglycerin" is unfortunate, since the substance is glyceryl trinitrate, $C_3H_5(NO_3)_3$. It has a freezing point of 11° C. (52° F.). When frozen it is less sensitive to shock, and some charges may escape detonation and be set off later with disastrous results. Tetranitrodiglycerin, nitrated sugars, nitrated glycols, and mixed esters of nitric and hydrochloric acids are also used along with nitroglycerin, both for the purpose of lowering freezing points and because they are also satisfactory explosives.

Nitroglycerin is used only to a very limited extent in its liquid state because of its extreme sensitiveness to shock, the chief use of the liquid material being in "shooting" oil wells. It is usually incorporated with other explosives, with oxidizing agents, and combustible materials in the various grades of "dynamite." No modern dynamites contain inorganic absorbents such as infusorial earth.

What is known as "straight" nitroglycerin dynamites vary in nitroglycerin content, the grades being 15%, 20%, 25%, and so on up to 60%. They all contain sodium nitrate and small amounts of calcium or magnesium carbonate. The combustible material is approximately constant, varying only from 14% to 20%. In the higher-strength dynamites it is all wood meal, but below "40% strength" flour and sulfur are included.

Low-freezing dynamites vary from 30% to 60% strength, this value referring to the total organic esters present. These are made up of approximately two-thirds nitroglycerin and one-third "nitrosubstitution compounds." Sodium nitrate, combustible material, and an alkali earth carbonate are included.

Gelatin dynamites contain no gelatin, the term being used to describe the physical properties of the explosive. Small amounts of nitrocellulose are used so that the nitroglycerin forms a colloidal jelly. The amount of combustible material is considerably lower, but the other components are much the same.

"Ammonia dynamites" contain ammonium nitrate in amounts from 15% to 30%. A "30% strength" ammonia dynamite, for example, is made up of 15% nitroglycerin and 15% ammonium nitrate. The other components are sodium nitrate, combustible material, and either calcium carbonate or zinc oxide. Low-freezing ammonia dynamites contain small amounts (3% to 6%) of nitrosubstitution compounds.

Nitroaromatic Compounds. This very important group of high explosives has been discussed in the previous chapter. They are in the main quite pure and stable solids, and are used either alone or with ammonium nitrate. The raw materials from which they are made are the same as those from which most synthetic dyestuffs are produced, and the equipment necessary for their manufacture is practically the same as that used in making dye intermediates from the starting substances or "crudes." The close relationship between the synthetic dye industry and the explosives industry is thus quite apparent.

IGNITING AND DETONATING MATERIALS

In order to initiate an explosion it is necessary to employ heat or violent impact. Propellants need only to be ignited by a flash of flame. The ignition of propellants varies with the type of weapon used. Small arms ammunition is ignited directly by the flash from the percussion cap. In ammunition for cannon the action of the percussion primer cap must be supplemented by a charge of black powder. In small cannon where a cartridge case is used, the black powder is confined in the "cannon primer," but in large cannon one or more bags or pads of black powder are put in after the charge of propellant has been loaded against the shell.

Low explosives used in blasting are ignited by fuse, which is ordinarily a woven tube containing a core of black powder. If the fuse is exposed to moisture or even immersed in water, it is necessary to use

a fuse with a waterproof outer coating around the woven tube. High explosives require the shock imparted by a detonator. As noted before, a small amount of detonator is often used with a booster charge of a less sensitive material. This has a relatively high velocity of detonation, which in turn sets off the main charge of high explosive. The initiation of an explosion is accomplished by the use of percussion caps and black powder fuses for flame ignition, and by detonators and detonating fuses where a shock is necessary.

The most important substances used as detonators are mercury fulminate, $\text{Hg}(\text{ONC})_2$, and lead azide, PbN_6 . Other materials used in making ignition caps and detonators are potassium chlorate, antimony sulfide, sulfur, mealed black powder, guncotton dust, powdered glass, and various glues, binders, and protective substances. Mercury fulminate is usually used in percussion caps with about four times its weight of such substances as potassium chlorate and antimony sulfide. When the explosion is initiated by shock, mercury fulminate is the chief constituent of the detonator. Mixtures of 80% fulminate and 20% potassium chlorate and also 90:10 mixtures are used. Tetryl and T.N.T. are also employed along with fulminate. Booster charges of tetryl are often used to carry the shock from the detonator to the main body of high explosive. Detonators are primarily copper tubes or capsules, closed at one end, which are filled with the detonating mixture. These are ignited by attaching them to ordinary fuse or more commonly by the use of a "bridge wire" of platinum or iridium connected with the firing circuit of copper wires. High explosive shells are caused to burst by the use of percussion caps or time fuses. Detonating fuse, which has only limited use, consists of tubes containing high explosive. Large tubes may be filled with powdered or molten materials of the nature of T.N.T. or picric acid, which are then drawn out to the smaller diameter required.

In addition to chemical analyses of the original components of explosives and of the finished products, numerous physical tests have been rigidly standardized. Space does not permit discussion of these tests, but it may be said that they have to do mainly with the force and heat of explosion, the pressure developed, the sensitiveness of the explosive to heat and shock, and the capacity of the explosive to ignite inflammable and explosive mixtures.

CHAPTER XXVII

PAINTS AND VARNISHES

The surfaces of wood, metal, and other materials of construction are covered and protected largely by coatings applied in thin layers in the fluid state, which subsequently change into elastic and impervious films. These coatings for the most part may be described by the two general terms "paints" and "varnishes." A paint produces an opaque coating because of the presence of solid materials known as pigments. A varnish is a clear coating material and is generally employed where it is desired that the surface to be protected remain visible. If a pigmented surface is quite smooth and glossy, the coating is often called an "enamel." Such materials should not be confused with the silicate coatings fused on the surface of metals. Originally, thin transparent finishes on metals were referred to as "lacquers." Shellac in alcohol and dammar in turpentine or petroleum spirits, both of which are "spirit varnishes"; nitrocellulose together with resins, plasticizers, solvents, and diluents; and a coating made from the sap of an Oriental tree were all called lacquers, each term being properly qualified. Since 1924 the term lacquer has been generalized to include all finishes, either clear or pigmented, which contain cellulose nitrate or cellulose acetate, and which dry by evaporation. The pigmented coatings are also called lacquer enamels.

Paint materials may be divided into pigments, vehicles, and driers. The pigments are solids and make up the larger part of the paint film. The vehicles include the solvents that serve to permit the ready and even application of the paint and subsequently evaporate, and oils, which harden by virtue of chemical changes and bind together the pigments into a continuous film. In enamels and some varieties of paint, synthetic and natural resins are incorporated in the oils and are thus also vehicles. Driers are catalysts that are used in small quantities to accelerate the hardening of the coating film.

Varnishes made up only of resins and thinners are known as spirit varnishes. When oils are also present they are called oleoresinous or oil varnishes.

PAINT AND VARNISH MATERIALS

Some of the materials used in the manufacture of paints and varnishes have been described in previous chapters. In general they include pigments, oils, resins, solvents, and driers.

Pigments. The bulk of pigments used in protective coatings are white. Colored pigments are primarily employed to produce the desired shade and tint in paint, although they have in themselves hiding power and ability to give mechanical strength to the film. Lead, zinc, and titanium compounds comprise the larger part of all paint pigments.

LEAD COMPOUNDS. What is known as *white lead* is essentially a basic lead carbonate. It may be represented by the formula: $2 \text{PbCO}_3 \cdot \text{Pb(OH)}_2$, but whether it is a simple chemical compound or not is immaterial. It is made from high-grade lead by the action of dilute acetic acid, hydrolysis of the normal acetate to a basic acetate, and conversion of this substance by the action of carbon dioxide to the basic carbonate. In a widely used process the lead is cast in perforated plates known as "buckles," which are charged into a series of clay pots containing dilute acetic acid. The liquid does not come in direct contact with the lead, being held in a sort of well in the bottom of the pot. The pots are arranged in tiers separated by boards, and are surrounded by spent tanbark. Fermentation and probably other chemical changes take place in the bark, resulting in the formation of the necessary carbon dioxide. The heat of these reactions slowly vaporizes the acetic acid. Finely divided lead produced by spraying may be placed in dilute acetic acid and exposed to the action of carbon dioxide from burning coke. This second process is often continuous, the lead being fed into one end of a long, horizontal, rotating cylinder, passed through counter current to the carbon dioxide, and the finished pigment being discharged at the opposite end.

Some white lead is made by an electrolytic process in which lead anodes are dissolved in a solution containing the requisite amount of carbonate ions for precipitating white lead. Carbonate ions diffuse through a diaphragm to maintain the necessary concentration. Hydrogen and sodium hydroxide are formed at iron cathodes. The caustic solution is recarbonated and returned. The precipitate is settled, filtered, washed, and dried.

The white lead made by either of the first two processes is freed from unchanged lead, ground very fine, screened through fine-mesh cloth, and sized by its rate of settling in water. It is freed from a part of its water in thickeners, and is either marketed dry or mixed with about 8% of its own weight of linseed oil. The "lead-in-oil"

product is not freed from water by drying but simply by the displacement of water by oil. In 1929 the production of basic lead carbonate in the United States amounted to 147,000 tons.

Basic lead sulfate, also often called *sublimed white lead*, is a mixture of varying amounts of lead sulfate and basic lead sulfate, $2 \text{PbSO}_4 \cdot \text{PbO}$. Its freedom from color and its effect on the drying rate of paints containing it indicate that it contains little or no free litharge, PbO . It is made by heating lead sulfide ore concentrates at a high temperature in the presence of an excess of air, cooling the gases, and removing the resulting solid product by dust collectors, usually of the bag filter type.

What is known as *sublimed blue lead* is also obtained from lead ore and is made up of lead oxide, lead sulfite, lead sulfide, and carbon. It is particularly valuable as a paint on metals on account of its rust-preventing effects.

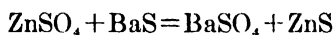
Minium, or lead orthoplumbate, has the formula, Pb_3O_4 , and is generally called *red lead*. It is formed by heating litharge, PbO , to a dull red for a long time in the presence of air. It is the standard pigment in paints used in the first coat on structural steel.

Lead chromate is made by the action of soluble dichromates on soluble lead salts such as the acetate. The color varies from pale yellow through orange to red, depending on the basicity of the material and the amount of lead sulfate present. *Chrome yellow* and *chrome red* both contain lead chromate. *Chrome green* is a mixture of chrome yellow and a blue pigment, ordinarily *Prussian blue*.

ZINC COMPOUNDS. *Zinc oxide*, ZnO , is made either by vaporizing slab zinc in a furnace and burning the vapors by letting them come in contact with the oxygen of the air (French process), or by reducing zinc ore with powdered coal and burning the zinc vapor with air to oxide, thus producing zinc "smoke," without isolating the metal (American process). In either case the oxide is recovered in flues followed by bag filters. The product is so extremely finely divided that it is not possible to refer to it in terms of mesh. The highest-power microscope is necessary in order to see the outline of the individual particles. It thus produces a very smooth finish. Zinc oxide is responsible for a high degree of durability in the paint film, and being practically impermeable to ultraviolet light serves to retard very greatly the decomposition of the hardened oil of the film. It is said to have the power of greatly lessening the effect of mildew. Since zinc sulfide is white, the action of hydrogen sulfide produces no darkening or discoloration in zinc oxide paint films. Zinc oxide holds

second place among white pigments produced in the United States, amounting in 1929 to 161,000 tons.

Zinc sulfide itself is a valuable pigment with high hiding power and the ability to retain luster in white and tinted enamels on exposure. The most widely used of all pigments is *lithopone*, since 206,000 tons of this material were made in this country in 1929. The term refers to a mixture of barium sulfate and zinc sulfide. The product is made by mixing solutions of barium sulfide and zinc sulfate, which results in the simultaneous precipitation of zinc sulfide and barium sulfate.



The product contains about 28% zinc sulfide and 72% barium sulfate. The crude lithopone is not suitable for use as a pigment. It is washed, filtered, dried, heated to redness in a muffle furnace, quenched in water, ground wet, dried, and finally ground dry. It is highly resistant to discoloration, to the action of mildew, and to penetration by ultra-violet rays. Like zinc oxide it is extremely finely divided. In recent years, "high-strength lithopones" are available which contain higher percentages of zinc sulfide (up to 50%) mixed either with barium sulfate or calcium sulfate, and consequently provides higher hiding power than ordinary lithopones.

TITANIUM COMPOUNDS. *Titanium dioxide*, TiO_2 , is a very opaque white pigment that has come into increasingly great use, particularly in nitrocellulose and quick-drying lacquer enamels. High-strength lithopones often contain 15% or more titanium dioxide in order to secure greater opacity. Titanium dioxide is also precipitated on barium sulfate and calcium sulfate, these pigments being widely used in paints, enamels, lacquers, and interior wall coatings. The titanium pigments are highly resistant to chemical action, permitting the use of acid vehicles. Being quite impermeable to light, they give great durability to paint films containing them.

MISCELLANEOUS PIGMENTS. In addition to the compounds of lead, zinc, and titanium there are a number of substances, mainly colored, that are used as paint pigments. Among these are the following. *Prussian blue*, ferric ferrocyanide, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, is made by mixing a solution of ferrous sulfate with a solution of alkali ferrocyanide and oxidizing the product with hypochlorites or chlorates. An artificially produced double silicate of sodium and aluminum containing sodium sulfide is called *ultramarine*. Various iron compounds are used as pigments, among which are *Venetian red*, made by heating ferrous sulfate and lime together, and *Indian red*, which is the product of calcining

ferrous sulfate. The latter pigment is also made from native iron ores. Cadmium sulfide and cadmium selenide are often mixed with barium sulfate much after the fashion of zinc sulfide in the lithopones, and these pigments may be referred to as *cadmopones*. They vary in color from red to yellow. One of the best known is *cadmium yellow*. Carbon is the chief component of black pigments. These include *carbon black*, better known as "gas black"; lampblack, an oil gas residual; and *ivory black*, an expensive artists' color with great tinting power made by calcining ivory chips. A variety of native minerals are used as pigments, among them being *umber*, a clay tinted with ferric and manganic oxides; *sienna*, a darker material because of great amounts of iron and manganese; *ocher*, which is either clay or calcium carbonate containing small amounts of ferric oxide; and *Prince's Metallic Brown*, an iron ore high in silica and alumina.

Lakes, as explained in another chapter, include mixtures of dyes and inert pigments, metallic salts of dyestuffs containing sulfonic acid groups, and dyes adsorbed on inert substances such as alumina. All manner of colors and shades are obtained by the use of organic dyes. It is essential that the colored material should be insoluble in oil and solvents as well as in water.

REINFORCING OR AUXILIARY PIGMENTS. Materials used in paint for special purposes, such as giving mechanical strength to the film or preventing its spreading too rapidly, are known as reinforcing pigments, extenders, or inerts. When used in reasonable amounts and for special purposes they are not regarded as adulterants, but rather as valuable parts of the paint film. They possess almost no opacity in oil vehicles. If used in too large amounts as cheapeners they lessen the value of the paint out of all proportion to the quantity present. Among these reinforcing pigments are short-fiber asbestos, talc, china clay, silica, gypsum, and barytes.

Oils. As pointed out in another chapter, drying oils are glycerin esters of unsaturated fatty acids that form tough, elastic films under the influence of the oxygen of the air. These oils have very low vapor pressures and do not "dry" in the sense that they evaporate. The production and general properties of these oils have already been described.

Linseed Oil. The glycerides composing this oil are largely those containing two and three double bonds. This renders the oil highly reactive towards oxygen. During the oxidation, gases are given off composed of water vapor, carbon dioxide, and various aldehydes and acids, and a tough, plastic substance known as "linoxyn" remains. It

is softened to some extent by benzol, and is saponified by sodium hydroxide solutions. What is known as "boiled" linseed oil is not ordinarily boiled, but is merely "cooked" oil, its preparation including the addition of lead and manganese salts and heating at various temperatures ranging from 150° C. to 275° C. A more common variety of linseed oil used in paints and also called boiled oil is prepared by adding concentrated driers to raw linseed oil.

An industry that consumes considerable quantities of linseed oil is the manufacture of floor coverings called "linoleum." Linseed oil is heated with driers and allowed to drip over suspended sheets of thin, coarse cloth. As each layer is oxidized, more oil is applied until the sheets are as much as one inch thick. The cloth and linoleum skins are ground together and the pulp is heated with rosin and other resins in kettles. A tough, porous mass is the result, which is allowed to age for several weeks. It is then ground with powdered cork and spread by heavy steel rolls on burlap. After being kept warm (60° C.) for several weeks, the coating becomes hard and tough. Inlaid linoleum is made up of blocks of different colors that are pressed hot by rolls on burlap. Colored designs are printed on plain linoleums. Cork may be omitted and the linoleum cement rolled on asphaltum paper. This product is later painted and designs are printed on it.

Tung Oil. Raw tung oil has little value in paints and varnishes, since it dries with a whitish or "frosty" film. By heating it with driers it becomes a satisfactory material and is very widely used in all types of paints and varnishes. It forms hard, water-resistant films and has almost entirely replaced linseed oil in varnishes and enamels. Rosin cannot be used with linseed oil in varnish because the product turns white when wet with water. Rosin cooked in tung oil gives products which do not suffer from this handicap. Tung oil forms a gel very rapidly when heated to 250° C. to 350° C., and less rapidly at lower temperatures.

Other Oils. *Soya bean oil* is used to a great extent in interior white paints. Although the film it forms is not very hard, its presence aids in resisting the yellowing of the coating. *Rosin oil* is extensively used in printing inks. Marine oils such as *menhaden oil* and *sardine oil* are employed in making paints, particularly those which have to withstand both heat and exposure to the weather.

Natural Resins. "Recent resins" is a term that refers to products that are continually being made by natural processes and that are gathered and used as rapidly as they are formed. What are called "fossil resins" are the results of changes in natural products that have

been going on for periods of time varying from a few years up to hundreds of centuries. Certain resins may be obtained direct from the tree, but a more valuable product is found in the earth at the site of former forests of these same trees. Hence the same name may be applied both to recent and fossil resins.

Lac. The resin from which commercial shellac is produced is known as lac. It differs from all other natural resins in that it is a resinous exudation of an insect infesting various types of trees. The word in an East Indian language means one hundred thousand, and refers to the large number of insects that cover the trees. The insect when hatched attaches itself to a soft twig and begins to suck up the sap and to cover itself with a secretion which dries up about it. The twigs covered with lac are broken off and gathered as "stick lac." The lac is broken from the twigs and washed to remove a red coloring matter, which was once used as a dyestuff. After removal of wood and other foreign matter the resin is dried in small grains called "seed lac." Shellac is made by melting seed lac in flat cloth bags, scraping the molten material from the surface, stretching it on cylinders through which hot water circulates, removing specks and imperfections, and breaking up the cooled sheets into flakes. In addition to moisture and wax, the chief components of crude lac are esters of aleuritic acid, $\text{CH}_2\text{OH}(\text{CH}_2)_5\text{CHOH}-\text{CHOH}(\text{CH}_2)_7\text{COOH}$. About 90% of commercial shellac comes from northeastern India.

Dammar. The term "dammar" is a generic Indian name for various resins, but the product that appears on the market is derived from a certain variety of coniferous tree in East India, Java, Sumatra, and Borneo. As it exudes from the tree it is soft, viscous, and possesses a highly aromatic odor. When exposed to the air it dries to an odorless, brittle, transparent, straw-colored solid. It is very extensively used as an ingredient of nitrocellulose lacquers.

Rosin. The residue that remains after the removal of volatile liquids from the collected exudations of pine trees is known as "colophony" or "rosin." It is largely abietic anhydride. Its uses in making soap and in the paper industry are discussed elsewhere. Calcium resinates are used in the varnish industry, rosin being treated with lime. Up to a few years ago, rosin was used only in the cheaper grades of varnish. It is now an important ingredient of high-grade varnishes. This change is due to its use with tung oil, which has already been described, and to its ability to form glycerin esters (ester-gum).

Ordinary *ester-gum* is the result of the reaction between rosin and glycerin. Since rosin is mainly an acid anhydride and glycerin is a

polyhydric alcohol, esterification can be readily brought about. The product is formed under the influence of heat. The acidity of the resin, and the varnish prepared from it, is thus reduced, allowing its use with basic pigments. Ester-gum also yields varnishes that are harder and more waterproof when cooked with tung oil than those made from rosin. Glycerides of Congo copals are also made and sold today.

Copals. The term "copal" is somewhat vaguely used for a number of resins that resemble each other in physical properties but which are different in constitution. Both *Manila* and *Sierra Leone* copals are obtained direct from the tree, but most copals are fossil resins. The hardness of these materials varies with their age. Raw copals are for the most part not on the market, but are used in the Orient in crude varnishes. *Zanzibar* copal is found imbedded in the ground at a depth up to four feet and in lumps that rarely weigh over a few ounces.

The most important of the fossil resins are *congo*, *pontianak*, and *kauri*. New Zealand is the source of *kauri*, which is dug from the earth, often far from living *kauri*-pine trees and where previously there were forests. It is found in lumps from one to eight inches in diameter and varies from nearly colorless and translucent material up to an amber yellow or brown color.

Synthetic Resins. Most of these materials have already been discussed in another chapter, and will be taken up here only as paint and varnish materials. These substances have revolutionized the varnish industry and are becoming increasingly important in paints. The new materials are of a number of types, including *phenol-formaldehyde resins*, *alkyd resins*, *chlorinated diphenyls*, *vinyl acetate* and *vinyl chloride* combinations, *cumarone* (*cumar*) and *indene resins*, and other types made from petroleum. These resins differ in their properties from molding resins, being soluble in paint and varnish oils such as tung oil. Varnishes made with these resins dry much more rapidly, and their durability on exposure and their resistance to moisture, alkalies, and acids are also greatly in advance of the fossil resin varnishes.

Bitumens. Naturally occurring asphalt, harder substances of the same nature as *gilsonite* and *grahamite*, coal-tar pitches, petroleum asphalt, and fatty acid pitches may be classed together as bituminous materials. They are used in making paints for the outer coats on structural steel and as ingredients in the baking varnishes or "japans" that coat automobile fenders.

Cellulose Nitrate. As stated in another chapter, cellulose nitrate and to a limited extent cellulose acetate are used as components of

industrial finishes now very generally known as lacquers. The cellulose nitrate is of about 12% nitrogen content and is soluble in a variety of organic liquids, largely alcohols and esters. Until recent years, cellulose nitrate solutions were too viscous for use in coatings that were applied by brushing or spraying, but by heating water suspensions of the cellulose nitrate under pressure, the viscosities of its solutions were so reduced that this material has become one of the most important ingredients of protective coatings.

Solvents or Thinners. The function of solvents is to dilute the paint and increase its flowing quality. A good thinner must not be so volatile that it escapes before brush marks have time to disappear, and at the same time it must evaporate rapidly enough to give the film an opportunity to begin hardening very soon after application. The term "solvent" in the modern lacquer industry is restricted to those liquids that will dissolve cellulose nitrate; other liquids are thinners or diluents.

Turpentine. What is known as "gum turpentine" is an exudation from living pine trees; "wood turpentine" refers to material obtained from seasoned pine wastes by steam distillation. The production of wood turpentine has been described in another chapter. Gum turpentine is collected by cutting away the bark and hacking the surface of living trees and collecting the exudation in earthenware cups by means of inclined metallic gutters. The hacked surface is slowly increased during the collecting season. When the liquid ceases to run, the hardened material that has collected on the surface is scraped off. The exudation is not sap, which is in a separate system of cells lying still deeper in the trunk of the tree. Products of the material so obtained are classed together as "naval stores."

The crude exudation is distilled from copper stills equipped for direct heating and the introduction of steam. When all volatile material has been removed the water is boiled out of the residue, which is rosin. About 20% of the material charged into the still is the volatile product known as "spirits of turpentine," which is the paint and varnish solvent commonly called "turpentine." Its principal component is pinene, $C_{10}H_{16}$. This substance is related to cymene, which is paramethylisopropyl benzene. Pinene exists in three stereoisomeric forms, two of them being optically active, and all of them boiling at $150^{\circ} C$. Dipentene, which is another product of the naval stores industry, is finding increasing use as a high solvent power thinner to improve the flow and leveling qualities of paints.

Petroleum Distillates. For many purposes, petroleum distillates,

known as "mineral spirits" and boiling in the same range as spirits of turpentine, are used as solvents. Not enough turpentine is produced in the world to meet half of the paint and varnish requirements of the United States. A more volatile product called "varnish makers' and painters' naphtha" also finds use in this industry. Several special fractions of petroleum are produced to match the boiling points of the aromatic hydrocarbons such as toluene and xylene.

Aromatic Hydrocarbons. Benzene is seldom used as a solvent, and attempts are being made to eliminate it as a paint and varnish remover. This is due to its toxic properties. The use of toluene, xylene, and high flash solvent naphtha, all coal-gas by-products, has increased very much in recent years in connection with synthetic resins of the phenolic and alkyd types.

Denatured Alcohol. Suitably denatured ethyl alcohol is the standard solvent for resin lacquers and shellac. It also has a limited use in nitrocellulose lacquers.

Miscellaneous Solvents. As indicated in another chapter, a considerable variety of organic liquids, some of them products of fermentation and others the result of synthetic processes, are used as solvents, particularly in connection with nitrocellulose lacquers. These include butyl and amyl alcohols, glycol ethers such as Cellosolve, ethyl, butyl, and amyl acetates, ethyl lactate, butyl propionate, hydrogenated petroleum derivatives, acetone, and many others.

Driers. Driers are substances that function as catalysts to accelerate the oxidation of paint and varnish oils and the hardening of the film. Any compounds of lead, cobalt, manganese, and iron that are capable of solution or colloidal dispersion in oils may function as driers. Manganese and cobalt are much more rapid in their action than lead. Combinations of lead and manganese, of lead and cobalt, or of all three, are still more rapid in their action. Based on the weight of oil, lead is present to the extent of 0.5% and manganese to 0.02% to 0.05%. Salts of the metals are often heated with linseed and other drying oils to temperatures ranging from 150° C. to 275° C. Instead of preparing the drier in the entire quantity of the oil, concentrated products may be made by heating inorganic salts of these metals with small quantities of resin or oil, or by the action of soluble metal salts on sodium resins and linoleates. The concentrated driers are known as japan driers and are dissolved in turpentine before being mixed with oils in paints and varnishes. Recently lead, manganese, cobalt, and zinc salts of the naphthenic acids of petroleum are being employed as driers. They are much more soluble in mineral

spirits, oils, and varnishes, and are much closer to molecular dispersions than the relatively large colloidal aggregates formed by resins or linoleates.

PAINTS

At one time most paints were made from the dry ingredients, oils, and solvents just before they were applied, the mixing being done by the painter. This practice meant a great variation in composition and quality according to individual skill. Modern machinery has made possible the manufacture of mixed paints of high quality. The solids are stored in bins and delivered in the desired quantity by gravity from automatic weighing hoppers. Rotary mixers combine the oil and the pigment. It is also common practice to grind the pigment in oil in chasers, between stone or steel plates in buhrstone mills, with rolls, or in ball mills, the buhrstone mill being most commonly used. Additional oil and thinner are then added in rotary mixers.

Although paints on metal need to be highly impervious to moisture, they should not be absolutely so on wood, since some moisture must escape from the wood. They must be elastic because of the relatively great expansion of wood when it becomes moist and its contraction due to loss of absorbed moisture under dry conditions. The spreading rate is important, this value varying with different pigments. An average paint will cover 300 to 400 sq. ft. per gallon. The hiding power of a pigment, or its opacity, depends on the refractive index of the pigment as related to that of the oils and other vehicles that remain in the film. Linseed oil has a refractive index of 1.48. A pigment with a refractive index of 1.66 has little hiding power; one with a refractive index of 2.10 has high hiding power. The nature of the solvent is intimately related to its power to hold pigments in suspension. Recent studies on liquids composed of polar, nonpolar, and polar-nonpolar molecules show that they are very differently adsorbed on pigments, and that the extent of dispersion depends on the polarity of the liquids used. The extent of "wetting" of a surface by a paint or varnish depends on such factors as electrical charge, surface tension, degree of polymerization, and gel dispersion. All ingredients should be chemically as resistant as possible in order to withstand the action of sun, rain, and air. Resistance to penetration of ultraviolet light is a most valuable asset of a pigment.

The covering of metal surfaces by paint in order to protect them from corrosion involves careful choice of materials. Both air and moisture are necessary before iron corrodes. Since it is impossible to

prevent the penetration of some moisture through a paint film, it is necessary to protect the metal by various pigments that will inhibit corrosion. Red lead has been for many years a standard pigment used in "primers," or first coats, on structural steel. Zinc chromate, used either alone or with iron oxides and other pigments, has shown unusual value as an anticorrosion primer. Other pigments used in rust-resisting paints are zinc dust with zinc oxide, blue lead, iron oxide with chromates such as zinc and lead, and metallic lead. On the other hand, it is possible to stimulate corrosion by the use of pigments that are soluble in water such as gypsum, acid-forming pigments, and conducting pigments like graphite. In order to exclude moisture as far as possible, fossil resins and bituminous materials have been used for many years. More modern waterproof and corrosion-resisting coatings have been based on the concentrated phenolic resin varnishes.

Fire-resisting paints contain considerable amounts of low fusion silicate mixtures or boric acid. These materials will fuse and thus protect the wood from oxidation even though slow charring takes place. No paint can make wood fireproof; but it may serve to hinder its ignition.

VARNISHES

Leighou defines varnishes as "resinous solutions applied to surfaces to produce hard, lustrous, and generally transparent protective coatings." There are two general types: spirit varnishes and oil varnishes.

Spirit Varnishes. Shellac is the main ingredient of spirit varnishes. The usual solvent is denatured grain alcohol. The coating produced by a spirit varnish is essentially the resin, since the solvent evaporates. Shellac forms a brittle coating, but it may be made more elastic by the use of oil or oil varnishes. Dyes may be used to produce tints in spirit varnishes. The surface coated by such varnishes cannot be washed with soap or other alkaline solutions.

Oil Varnishes. Resins, drying oils, and thinners are the principal components of oil varnishes. A small amount of driers (salts of lead, manganese, and cobalt) is usually cooked into the batch or added in soluble liquid form later to the extent of 0.1% to 0.5% of the weight of the oil. The thinner is usually mineral spirits, although turpentine, xylene, solvent naphtha, dipentene, and similar solvents may be added in minor quantities, depending upon the solubility of the resin-oil "cook." The unit generally employed in discussing varnish batches is on the basis of the number of gallons of oil to 100 lb. of resin. A

"long" varnish is one with 20 to 100 gallons of oil, and is therefore generally durable and flexible. A "short" varnish has 15 gallons or less of oil, and owing to its relatively high resin content is harder, more brilliant, and not so flexible or elastic.

Up to about 1920 only natural resins were used in varnish making. The general procedure included melting the resin, pouring into it linseed oil containing driers, heating the mixture to thorough incorporation, cooling somewhat, adding thinners, allowing to stand, and filtering or centrifuging for clarification. Such a varnish would require from 24 to 72 hours to dry, and would be unsatisfactory with regard to durability, waterproofness, and resistance to wear and corrosion compared with the varnish of today.

Since 1924 the manufacture of varnishes and enamels has been completely changed because of the introduction of synthetic varnish resins. The phenol-formaldehyde resins were formerly modified with rosin or ester-gum, but in recent years completely oil-soluble phenolic resins are available. The alkyd resins that are used in oil varnishes are made by modifying the reaction between glycerin and phthalic anhydride by means of castor oil or the fatty acids of drying oils. The most durable finishes are today made to dry in from $\frac{1}{2}$ hour to 4 hours.

The new-type varnishes employ mainly tung oil with the synthetic resins. These are cooked together as it is unnecessary to melt or "run" the resin to make it soluble. Probably 75% or more of the varnish made today is prepared with such resins as rosin, ester-gum, and synthetic resins none of which need to be run. In modern varnish manufacture using synthetic resins most of the oil and resins are heated together. The temperature is raised over a controlled fire, and when the desired consistency is reached the kettle is pulled from the fire and any remaining oil is added. After the material has cooled to temperatures ranging from 375° F. to 450° F., the thinner, usually petroleum spirits, is added. Driers are ordinarily put in during the cooking operation. If a very light-colored varnish is desired, liquid driers are added, either before or after the varnish is thinned.

NITROCELLULOSE LACQUERS AND LACQUER ENAMELS

The modern protective coatings based on "low-viscosity" cellulose nitrates have been discussed in another chapter. Since 1925 or 1926 the finishing coats of automobiles have been almost entirely lacquer enamels, with the exception of the black baking japans on the fenders.

Furniture today is largely coated with transparent lacquers. The main components of such lacquers are: the nitrocellulose; the resin (ester-gum, dammar, shellac, or synthetic resin); the plasticizer (castor oil or high-boiling esters such as dibutyl phthalate or tricresyl phosphate); the thinners consisting of active solvents (such as butyl, ethyl, and amyl acetates, alcohols, ethylene glycols, glycol ethers); and diluents (such as toluene, xylene, and petroleum hydrocarbons). The thinners are usually very volatile, and the product is applied by spraying. In brushing lacquers, higher-boiling and slower-evaporating solvents are increased in the formula.

The lacquers are prepared by dissolving the cellulose nitrate in butyl or ethyl acetate, dissolving the resins in toluene, and combining the solutions with plasticizers and further thinners in mixers. When pigments are ground in to form lacquer enamels, the pigment is usually first ground in suitable mills in the mixed resin solutions and in plasticizers.

JAPANS

Coatings applied to metal and hardened by heat are known as "japans." Bituminous materials are the chief components of japan finishes. With them are included resins, paint oils, and solvents such as toluene and solvent naphtha. Such finishes are commonly applied by dipping metal articles into them, and are hardened by baking at temperatures of the order of 300° F. The hardening is probably due to polymerization reactions, oxidation being a minor phenomenon. Japans are chiefly used on the fenders of automobiles.

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